UNIVERSITY OF HAWAII
LIBRARY
DEC 29 '55

# ADVANCES IN PHYSICS

## A QUARTERLY SUPPLEMENT
## of the
## PHILOSOPHICAL MAGAZINE

EDITOR
PROFESSOR N. F. MOTT, M.A., D.Sc., F.R.S.

EDITORIAL BOARD
SIR GEORGE THOMSON, M.A., D.Sc., F.R.S.
PROFESSOR A. M. TYNDALL, C.B.E., D.Sc., F.R.S.
SIR LAWRENCE BRAGG, O.B.E., M.C., M.A., D.Sc., F.R.S.

VOLUME 4 OCTOBER 1955 NUMBER 16

PRICE per part 15*s*. 0*d*.
PRICE per annum £2 15*s*. 0*d*. post free

PRINTED AND PUBLISHED BY TAYLOR & FRANCIS, LTD
RED LION COURT, FLEET ST., LONDON E.C.4

QC1
A36

JOURNAL OF

# ELECTRONICS

A "PHILOSOPHICAL MAGAZINE" ASSOCIATED JOURNAL

*Editor :* J. THOMSON, M.A., D.Sc., M.I.E.E., F.Inst.P.

*Consultant Editor :* Professor N. F. Mott, F.R.S.

CONTENTS—NO. 2, SEPTEMBER 1955

Speculations on the Energy Band Structure of Zinc-Blende-Type Crystals. By F. Herman (*RCA Laboratories, Princeton, New Jersey, U.S.A.*).

Bond Relationships in Diamond-type Semiconductors. By C. H. L. Goodman (*Research Laboratories, The General Electric Co. Ltd., Wembley, England*).

The Validity of the Hydrogen-like Approximation for Impurity Levels. By G. Rickayzen (*Services Electronics Research Laboratory, Baldock, Herts.*).

Photovoltaic and Photoconductive Theory Applied to InSb. By T. S. Moss (*Radio Department, Royal Aircraft Establishment, Farnborough*).

The Photoelectromagnetic Effect in Indium Antimonide. By C. Hilsum, D. J. Oliver and G. Rickayzen (*Services Electronics Research Laboratory, Baldock, Herts.*).

Some Implications of the Small Energy Gap and Small Effective Electron Mass in InSb. By J. W. Allen (*Ericsson Telephones Ltd., Beeston, Nottingham*) and I. M. Mackintosh (*Department of Physics, University of Nottingham*).

Measurements of Diffusion Length in Indium Antimonide. By D. G. Avery and D. P. Jenkins (*Radar Research Establishment, Great Malvern, Worcs.*).

Accurate Measurements of Absorption in Indium Antimonide and Gallium Antimonide. By V. Roberts and J. E. Quarrington (*Radar Research Establishment, Great Malvern, Worcs.*).

A Study of the Conduction Band of InSb. By R. Barrie and J. T. Edmond (*Services Electronics Research Laboratory, Baldock, Herts.*).

The Electrical Properties of Indium Antimonide at Low Temperatures. By B. V. Rollin and A. D. Petford (*The Clarendon Laboratory, Oxford*).

The Magneto-resistance Effect in Indium Antimonide. By R. Mansfield (*Bedford College, London*).

A simple Method to Visualize Degeneracy of an Intrinsic Semi-conductor. By G. Busch (*Swiss Federal Institute of Technology, Zürich*).

Optical and Electrical Properties of GaAs, InP and GaP. By H. Welker (*Siemens-Schuckertwerke A.G., Erlangen*).

On the Degeneracy Effect in InAs. By R. Talley and F. Stern (*U.S. Naval Ordnance Laboratory, Silver Spring, Maryland, U.S.A.*).

Preparation and Electrical Properties of CdTe Single Crystals. By F. A. Kröger and D. de Nobel (*Philips Research Laboratories, N. V. Philips' Gloeilampenfabrieken, Eindhoven, Netherlands*).

The Preparation, Electrical and Optical Properties of Mg$_2$Sn. By W. D. Lawson, S. Nielsen, E. H. Putley and V. Roberts (*Radar Research Establishment, Great Malvern, Worcs.*).

Zone Melting of Decomposing Solids. By J. van den Boomgaard, F. A. Kröger and H. J. Vink (*Philips Research Laboratories, N. V. Philips' Gloeilampenfabrieken, Eindhoven, Netherlands*).

Thermoelectric Applications of Semiconductors. By H. J. Goldsmid (*Research Laboratories, The General Electric Co. Ltd., Wembley, England*).

Applications of Indium Antimonide. By I. M. Ross and E. W. Saker (*Services Electronics Research Laboratory, Baldock, Herts.*).

6 parts per volume—£1–0–0 per part

Subscription price per volume £5–10 *post free*, payable in advance

*Publishers*

TAYLOR & FRANCIS, LTD

RED LION COURT, FLEET STREET, LONDON, E.C.4

# CONTENTS

Perturbation Theory in Statistical Mechanics. By S. Nakajima, Department of Theoretical Physics, The University of Liverpool . . 363

A Survey of Irradiation Effects in Metals. By J. W. Glen, The Royal Society Mond Laboratory, Cambridge . . . . . . . 381

ADVANCES IN PHYSICS
A QUARTERLY SUPPLEMENT
of the
PHILOSOPHICAL MAGAZINE

VOLUME 4 OCTOBER 1955 NUMBER 16

# *Perturbation Theory in Statistical Mechanics*

By S. NAKAJIMA
Department of Theoretical Physics, The University of Liverpool

## § 1

IN statistical mechanics, if we take the canonical distribution, the free energy $F$ of any system is given by

$$\exp(-\beta F)=\sum_n \exp(-\beta E_n), \quad \beta^{-1}=\kappa T, \quad . \quad . \quad . \quad (1.1)$$

where $\kappa$ is the Boltzmann constant, $T$ the absolute temperature, and $E_n$ the $n$th eigenvalue of the Hamiltonian $\mathscr{H}$ of the system. As is well known, (1.1) can be expressed in terms of the trace of the so-called density operator $\exp(-\beta\mathscr{H})$

$$\exp(-\beta F)=\mathrm{Tr}\,[\exp(-\beta\mathscr{H})]=\sum_n\langle\Psi_n, \exp(-\beta\mathscr{H})\Psi_n\rangle. \quad (1.2)$$

This is obvious if the $\Psi_n$ are the eigenfunctions of $\mathscr{H}$. It is also valid if the $\Psi_n$ are *any* complete set of orthonormalized wave functions since the trace, i.e. the sum of diagonal matrix elements of an operator, is invariant under unitary transformations. In order to evaluate the free energy from (1.1), all eigenvalues of $\mathscr{H}$ have to be found by solving the Schrödinger equation, which is not feasible except for simple systems. In the form (1.2), on the other hand, use can be made of any convenient set $\{\Psi_n\}$. Even so, the exact evaluation of the trace is normally very difficult, and a number of approximate methods have therefore been developed. Among them, the Hartree method which at an early stage has been applied in the molecular field theory of ferromagnetism, is a simple example. A systematic study of this method was given by Hushimi (1940). As is shown in the Appendix, the method is based on the variation principle, i.e. the principle of maximum entropy.

Other approximate methods are more or less based on certain expansion theorems of the density operator $\exp(-\beta\mathscr{H})$. For instance, the straightforward expansion into a power series in $\beta$ has often been used in the high temperature region. One of the difficulties encountered in dealing with the density operator is the non-commutability of quantum mechanical variables which prevents the simple factorization of the exponential. If quantum fluctuations are expected to be small, the expansion into a power series in the Planck constant $2\pi\hbar$ may be available (Wigner 1932). Peierls (1932) also discussed a method of expansion into a power series of the non-commutability correction, by which he clearly showed how the diamagnetism of the free electron gas results from quantum effects. Kubo (1952) has proved a more general expansion theorem than these and applied it to the Heisenberg model of ferromagnetism.

The present article, however, is mainly concerned with the perturbative expansion. In actual applications, we often meet the case in which the Hamiltonian is composed of two parts: the unperturbed Hamiltonian $\mathscr{H}_0$, which is assumed to be simple enough to evaluate the free energy by (1.2), and the perturbation $\epsilon\mathscr{H}_\mathrm{I}$ which is small compared with $\mathscr{H}_0$,

$$\mathscr{H}=\mathscr{H}_0+\epsilon\mathscr{H}_\mathrm{I}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.3)$$

where $\epsilon$ is a small numerical parameter to indicate the order of magnitude. For such a Hamiltonian, it may be expected that a perturbation theory can be developed similar to perturbation theory in quantum mechanics. In fact, Peierls (1932) derived the perturbative expansion of the density operator $\exp(-\beta\mathscr{H})$, making use of quantum mechanical perturbation theory. He pointed out that the range of validity of statistical mechanical perturbation theory can be wider than that of quantum mechanical perturbation theory. A more direct expansion method has recently been studied by a number of authors, particularly by Schafroth (1951) and by Goldberger and Adams (1952). In the present article it is intended to give a general formulation of their theory, to show the connection with quantum mechanical perturbation theory, and also to give expressions suitable for the actual evaluation of the free energy.

For a system described by the Hamiltonian (1.3), the free energy will be expanded as

$$F=F_0+\epsilon F_1+\epsilon^2F_2+\dots \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.4)$$

In §§ 2 and 3, we shall show how to determine the $F_n$'s. In § 2, a symbolic method due to Kubo will be discussed, which is similar to the quantum theory of multiple scatterings. By this method it will be shown clearly that the difficulties which in quantum mechanical perturbation theory arise in connection with a degeneracy of energy levels (i.e. vanishing denominators) do not occur in statistical mechanical perturbation theory. In § 3, we shall discuss a more direct expansion, whose result is expressed in terms of the expectation values of the product operator

$$\mathscr{H}_\mathrm{I}\cdot\mathscr{H}_\mathrm{I}\dots\mathscr{H}_\mathrm{I}$$

with respect to the unperturbed canonical distribution $\exp(-\beta\mathscr{H}_0)$. This method seems more suitable for the actual evaluation of the free energy than the method of § 2. As an example we shall apply it to the electron–phonon interaction in non-superconducting metals.

In § 4, the diamagnetism of a charged gas will be treated by our method as well as by quantum mechanical perturbation theory. Formally this is a simple example for comparing both theories, although the problem is rather complicated from the physical point of view.

In § 5, a brief account of Schafroth's general method of dealing with diamagnetism will be given. Although this discussion is not directly concerned with perturbation theory, some important comments on the theory of diamagnetism, with particular reference to the Meissner effect, will be made. In particular it will be shown how macroscopic magnetic equations can be derived from the microscopic Hamiltonian by a method which is somewhat different from the conventional one (van Vleck 1932). The same problem is treated by the Hartree method in the Appendix.

## § 2

To derive the perturbative expansion of the density operator by means of a symbolic method due to Kubo let us start from Cauchy's theorem

$$\exp(-\beta\mathscr{H})=\frac{1}{2\pi i}\oint\frac{\exp(-\beta E)}{E-\mathscr{H}}\,dE. \quad . \quad . \quad . \quad . \quad (2.1)$$

Here the operator $(E-\mathscr{H})^{-1}$ should be understood in such a way that it gives the factor $(E-E_n)^{-1}$ when it operates on the eigenfunction $\Psi_n$ of $\mathscr{H}$, and the contour of integration is taken so as to enclose all eigenvalues $E_n$ (going along the real axis from $-\infty$ to $+\infty$ in the lower half plane and coming back in the upper half plane).

Now the poles in (2.1) are of course determined by the Schrödinger equation

$$(E-\mathscr{H})\Psi=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.2)$$

If, however, the Hamiltonian has the form (1.3), the operator $(E-\mathscr{H})^{-1}$ can be expanded as

$$\frac{1}{E-\mathscr{H}}=\frac{1}{E-\mathscr{H}_0}+\frac{1}{E-\mathscr{H}_0}\epsilon\mathscr{H}_{\mathrm{I}}\frac{1}{E-\mathscr{H}_0}$$
$$+\frac{1}{E-\mathscr{H}_0}\epsilon\mathscr{H}_{\mathrm{I}}\frac{1}{E-\mathscr{H}_0}\epsilon\mathscr{H}_{\mathrm{I}}\frac{1}{E-\mathscr{H}_0}+\ldots, \quad . \quad (2.3)$$

as is easily verified by multiplying both sides by $(E-\mathscr{H}_0-\epsilon\mathscr{H}_{\mathrm{I}})$. Inserting (2.3) into (2.1) and taking the matrix element with respect to the unperturbed eigenfunctions $\Phi_n$ belonging to the eigenvalues $W_n$ of $\mathscr{H}_0$, we have

$$\begin{aligned}\langle n|\exp(-\beta\mathscr{H})|m\rangle &\equiv\langle\Phi_n,\ \exp(-\beta\mathscr{H})\Phi_m\rangle\\ &=f_1(W_n)\delta_{n,m}+\epsilon\langle n|\mathscr{H}_{\mathrm{I}}|m\rangle f_2(W_n,W_m)\\ &\quad+\epsilon^2\sum_r\langle n|\mathscr{H}_{\mathrm{I}}|r\rangle\langle r|\mathscr{H}_{\mathrm{I}}|m\rangle f_3(W_n,W_r,W_m)+\ldots, \quad . \quad (2.4)\end{aligned}$$

where

$$f_\nu(W_1,W_2,\ldots,W_\nu)=\frac{1}{2\pi i}\oint\frac{\exp(-\beta E)}{(E-W_1)\ldots(E-W_\nu)}\,dE. \quad . \quad (2.5)$$

This is the expansion formula first obtained by Schafroth (1951). It is evident that there is no difficulty of vanishing energy denominators. For example if $W_\nu$ is equal to $W_1$,

$$\lim_{W_\nu \to W_1} f_\nu(W_1, \dots, W_\nu) = \frac{\partial}{\partial W_1} f_{\nu-1}(W_1, \dots, W_{\nu-1}). \quad . \ . \ (2.6)$$

In particular

$$f_1(W) = \exp(-\beta W),\ f_2(W, W') = \frac{f_1(W) - f_1(W')}{W - W'}, \quad . \ . \ (2.7)$$

etc. The expansion of the right-hand side of (1.2), using (1.3) and (2.4)–(2.7) is thus

$$\mathrm{Tr}\,[\exp(-\beta \mathscr{H})] = \sum_n \exp(-\beta W_n) - \epsilon\beta \sum_n \langle n \mid \mathscr{H}_{\mathrm{I}} \mid n \rangle \exp(-\beta W_n)$$
$$- \tfrac{1}{2}\epsilon^2 \beta \sum_{n,m} |\langle n \mid \mathscr{H}_{\mathrm{I}} \mid m \rangle|^2 \left( \frac{\exp[-\beta W_n] - \exp[-\beta W_m]}{W_n - W_m} \right) + \dots$$
$$. \ . \ . \ . \ . \ . \ (2.8)$$

The left-hand side of (1.2) is expanded as

$$\exp(-\beta F) = \exp(-\beta F_0) \left( 1 - \epsilon\beta F_1 + \frac{\epsilon^2}{2} (\beta^2 F_1{}^2 - 2\beta F_2) + \dots \right). \quad (2.9)$$

Comparing (2.9) with (2.8), one can successively determine the $F_n$. Thus

$$F = F_0 + \epsilon \Sigma \exp[\beta(F_0 - W_n)] \langle n \mid \mathscr{H}_{\mathrm{I}} \mid n \rangle$$
$$+ \frac{\epsilon^2}{2} \Big\{ \beta (\Sigma \exp[\beta(F_0 - W_n)] \langle n \mid \mathscr{H}_{\mathrm{I}} \mid n \rangle)^2$$
$$+ \Sigma |\langle n \mid \mathscr{H}_{\mathrm{I}} \mid m \rangle|^2 \frac{\exp[\beta(F_0 - W_n)] - \exp[\beta(F_0 - W_m)]}{W_n - W_m} \Big\} + \dots,$$
$$. \ . \ . \ (2.10)$$

with $$\exp(-\beta F_0) = \Sigma \exp(-\beta W_n).$$

This formula reduces to the well-known result of perturbation theory in quantum mechanics if we take the limit $\beta \to \infty$. For in this limit the free energy $F_0$ tends to the lowest unperturbed energy level $W_0$ and all $\exp(\beta(F_0 - W_n))]$ tend to zero except for $n = 0$. Thus we obtain the lowest energy of the perturbed system given by

$$E_0 = W_0 + \epsilon \langle 0 \mid \mathscr{H}_{\mathrm{I}} \mid 0 \rangle \epsilon^2 \sum_{n \neq 0} \frac{|\langle 0 \mid \mathscr{H}_{\mathrm{I}} \mid n \rangle|^2}{W_0 - W_n} + \dots \quad . \ . \ (2.11)$$

Quantum mechanical perturbation theory, when applied to the excited state $i$, gives the expression of the same form as (2.11), the index 0 being replaced by the index $i$. But this expression diverges if the system is degenerate ($W_n = W_i$, for $i \neq n$). We thus have either to take the principal value of the summation over intermediate states, or more reasonably but with great difficulty to find a suitable linear combination of unperturbed eigenfunctions to avoid the divergence. On the other hand, such a divergence does not occur in statistical mechanics, the vanishing energy difference in the denominator being cancelled by the vanishing difference of the Boltzmann factors in the numerator. Roughly speaking, the difficulty of vanishing energy denominators is smeared out by taking the statistical average. This means, however, that at low temperatures we must carefully test whether the divergence difficulty is only formal or of real physical importance. Unfortunately, it is often very difficult to find the precise mathematical conditions under which our perturbation theory can be applied, and we must more or less physically decide its validity.

A good example is the electron–phonon interaction in metals. As we shall see in § 3, $\mathscr{H}_0$ in this case is the energy of free electrons and free phonons, and $\epsilon\mathscr{H}_\mathrm{I}$ represents various processes in which one electron makes the transition by emitting or absorbing one phonon. These transitions are classified into two types: real transitions, which conserve the energy of the unperturbed system and thus lead to vanishing energy denominators, and virtual transitions which do not conserve energy. If the electron–phonon interaction is fairly weak (normal metals), the real transitions lead to the electric and thermal resistances as treated by the usual theory of conductivity, and thus do not have any appreciable effect on equilibrium properties of metals. Therefore perturbation theory can be applied to see what effect will be caused by the virtual transition on equilibrium properties of normal metals. This has been done by Buckingham and Schafroth (1954); they found that the velocity of sound and the electronic energy level density are modified by the interaction (see § 3). In superconducting metals, on the contrary, the electron–phonon interaction is too strong to be treated by perturbation theory; the real transitions in particular bring about a drastic change in the electronic states to such an extent that it eliminates even the residual resistance (Fröhlich 1953).

In concluding this section we would like to point out the similarity between our formalism and the symbolic treatment of scattering (Gell-Mann and Goldberger 1953). In the latter, assuming that the Hamiltonian of the free particle system $\mathscr{H}_0$ and the total Hamiltonian $\mathscr{H}_0+\epsilon\mathscr{H}_\mathrm{I}$ have the same continuous spectrum, the Schrödinger eqn. (2.2) can be rewritten in the integral form

$$\Psi=\Phi+\frac{1}{E-\mathscr{H}_0}\epsilon\mathscr{H}_\mathrm{I}\Psi, \qquad . \quad . \quad . \quad . \quad . \quad . \quad (2.12)$$

where $\Phi$ represents the incident wave

$$(E-\mathscr{H}_0)\Phi=0.$$

In scattering problems, the operator $(E-\mathscr{H}_0)^{-1}$ must be defined such that the second term in (2.12) represents the outgoing waves at infinity; in our formalism such a boundary condition does not exist. This is closely connected with the fact discussed above that the vanishing energy denominators do not lead to singularities. By iteration, (2.12) can be solved in the form

$$\Psi=\left(1+\frac{1}{E-\mathscr{H}_0}\epsilon\mathscr{H}_{\mathrm{I}}+\frac{1}{E-\mathscr{H}_0}\epsilon\mathscr{H}_{\mathrm{I}}\frac{1}{E-\mathscr{H}_0}\epsilon\mathscr{H}_{\mathrm{I}}+\ldots\right)\Phi, \quad . \quad (2.13)$$

which corresponds to (2.3). Here the factor $(E-\mathscr{H}_0)^{-1}$ represents the propagation of free particles and the factor $\epsilon\mathscr{H}_{\mathrm{I}}$ the scattering. It might be possible, therefore, to develop approximate methods in statistical mechanics which correspond to various approximations made in dealing with the multiple scatterings in (2.13).

## § 3.

In actual applications, it is not always convenient to take the explicit matrix representation, as has been done in § 2. There is another method of deriving the same expansion formula which, however, is expressed in terms of the expectation values with respect to the unperturbed canonical distribution :

$$\langle Q\rangle_{\beta}\equiv \mathrm{Tr}\,(\exp[-\beta\mathscr{H}_0]Q)/\mathrm{Tr}\,(\exp[-\beta\mathscr{H}_0)]. \quad . \quad . \quad (3.1)$$

Thus the actual calculation is reduced to evaluating these expectation values.

We first derive the perturbative expansion of the density operator $R(\beta)=\exp(-\beta\mathscr{H})$, which satisfies

$$\frac{\partial R(\beta)}{\partial\beta}=-\mathscr{H}R(\beta). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.2)$$

If the Hamiltonian has the form (1.3), (3.2) can be rewritten as

$$R(\beta)=\exp(-\beta\mathscr{H}_0)(1-\epsilon\int_0^{\beta}d\lambda\,\mathscr{H}_{\mathrm{I}}(\lambda)\exp[-\lambda\mathscr{H}_0]R(\lambda)). \quad . \quad . \quad (3.3)$$

This can be verified by differentiation using the definition of the operator $\mathscr{H}_{\mathrm{I}}(\lambda)$ :

$$\mathscr{H}_{\mathrm{I}}(\lambda)=\exp(\lambda\mathscr{H}_0)\mathscr{H}_{\mathrm{I}}\exp(-\lambda\mathscr{H}_0). \quad . \quad . \quad . \quad (3.4)$$

By iteration, (3.3) is solved in the form

$$R(\beta)=\exp(-\beta\mathscr{H}_0)\left(1-\epsilon\int_0^{\beta}d\lambda_1\mathscr{H}_{\mathrm{I}}(\lambda_1)\right.$$
$$\left.+\epsilon^2\int_0^{\beta}d\lambda_1\int_0^{\lambda_1}d\lambda_2\mathscr{H}_{\mathrm{I}}(\lambda_1)\mathscr{H}_{\mathrm{I}}(\lambda_2)+\ldots\right). \quad . \quad . \quad . \quad . \quad (3.5)$$

The similarity between our expansion and perturbation theory in quantum mechanics is obvious. In the latter, we are concerned with the operator $\exp(-it\mathscr{H}/\hbar)$, which is obtained from $\exp(-\beta\mathscr{H})$ if one replaces $\beta$ formally by $it/\hbar$. The same replacement, when applied to the expansion (3.5) and to the operator (3.4), leads to the well-known Dyson expansion and to the interaction representation of $\mathscr{H}_{\mathrm{I}}$, respectively, which are basic in modern quantum mechanics (Dyson 1949).

It is not convenient directly to take the trace of (3.5). Instead, following Goldberger and Adams, we start from the formula

$$\frac{\partial}{\partial\epsilon}\mathrm{Tr}\,(\exp[-\beta\mathscr{H}])=-\beta\,\mathrm{Tr}\,(\exp[-\beta\mathscr{H}]\epsilon\mathscr{H}_{\mathrm{I}}), \quad . \quad . \quad (3.6)$$

which can be verified by straightforward differentiation, expanding the exponential into an infinite series. Integrating (3.6) over $\epsilon$, we have

$$\mathrm{Tr}\,(\exp[-\beta\mathscr{H}])=$$
$$\mathrm{Tr}\,(\exp[-\beta\mathscr{H}_0])-\beta\int_0^{\epsilon}d\eta\,\mathrm{Tr}\,(\exp[-\beta(\mathscr{H}_0+\eta\mathscr{H}_{\mathrm{I}})]\eta\mathscr{H}_{\mathrm{I}}).$$

If the expansion (3.5) is applied to the integrand on the right, one obtains

$$\mathrm{Tr}\,(\exp[-\beta\mathscr{H}])=\mathrm{Tr}\,(\exp[-\beta\mathscr{H}_0])-\epsilon\beta\,\mathrm{Tr}\,(\exp[-\beta\mathscr{H}_0]\mathscr{H}_{\mathrm{I}})$$
$$+\frac{\epsilon^2}{2}\beta\int_0^{\beta}d\lambda\,\mathrm{Tr}\,(\exp[-\beta\mathscr{H}_0]\mathscr{H}_{\mathrm{I}}(\lambda)\mathscr{H}_{\mathrm{I}})+\ldots. \quad (3.7)$$

Comparing this with (2.9), we obtain the free energy corrections. The result is expressed in terms of the expectation values (3.1):

$$F=F_0+\epsilon\langle\mathscr{H}_{\mathrm{I}}\rangle_\beta+\tfrac{1}{2}\epsilon^2\Big\{\beta\langle\mathscr{H}_{\mathrm{I}}\rangle_\beta^2$$
$$-\int_0^{\beta}d\lambda\langle\mathscr{H}_{\mathrm{I}}(\lambda)\mathscr{H}_{\mathrm{I}}\rangle_\beta\Big\}+\ldots \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.8)$$

The explicit matrix representations of (3.5) and (3.8) agree with previous results (2.4) and (2.10), respectively.

As an example consider the electron–phonon interaction in normal metals. The Hamiltonian takes the form

$$\mathscr{H}_0=\Sigma\epsilon_k n_{\mathbf{k}}+\Sigma\hbar w s_0 N_{\mathbf{w}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.9)$$
$$\epsilon\mathscr{H}_{\mathrm{I}}=i\sum_{w\neq 0}C(\mathbf{w})a^*_{\mathbf{k}+\mathbf{w}}a_{\mathbf{k}}(b_{\mathbf{w}}-b_{-\mathbf{w}}^*). \quad . \quad . \quad . \quad . \quad (3.10)$$

Here $n_{\mathbf{k}}=a_{\mathbf{k}}^*a_{\mathbf{k}}$ and $N_{\mathbf{w}}=b_{\mathbf{w}}^*b_{\mathbf{w}}$ are occupation numbers of electrons with the wave vector **k** and of phonons with the wave vector **w**, respectively (we disregard the electron spin). $a_{\mathbf{k}}$, $a_{\mathbf{k}}^*$ are destruction and creation operators of electrons, and $b_{\mathbf{w}}$, $b_{\mathbf{w}}^*$ are those of phonons. They satisfy the well-known commutation and anticommutation rules:

$$[b_{\mathbf{w}},b_{\mathbf{u}}^*]_-=\delta_{\mathbf{w},\mathbf{u}},\quad [a_{\mathbf{k}},a_{\mathbf{l}}^*]_+=\delta_{\mathbf{k},\mathbf{l}}. \quad . \quad . \quad . \quad . \quad (3.11)$$

$\epsilon_k$ is the energy of a single free electron, $s_0$ the velocity of sound without interaction with electrons, and $C(\mathbf{w})$ the coupling constant. The observed sound velocity $s$ is shifted by a certain amount $\delta s$ from the unperturbed value $s_0$ because of the electron–phonon interaction

$$s(\mathbf{w})=s_0+\delta s(\mathbf{w}). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.12)$$

The change of self-energy of the phonon connected with this can be calculated by decomposing the total Hamiltonian into the form

$$\mathscr{H}_0+\epsilon\mathscr{H}_{\mathrm{I}}=\mathscr{H}_0'+(\epsilon\mathscr{H}_{\mathrm{I}}-\delta\mathscr{H}), \quad . \quad . \quad . \quad . \quad . \quad (3.13)$$

with

$$\mathscr{H}_0'=\Sigma\epsilon_{\mathbf{k}}n_{\mathbf{k}}+\Sigma\hbar w s N_{\mathbf{w}},\quad \delta\mathscr{H}=\Sigma\hbar w\delta s N_{\mathbf{w}}.$$

We regard $\mathscr{H}_0'$ as the unperturbed Hamiltonian, in which the phonon has the observed sound velocity $s$.

Now the expectation values of occupation numbers are well-known Bose and Fermi distribution functions:

$$\left.\begin{aligned}\langle N_{\mathbf{w}}\rangle_\beta &= f_p(\mathbf{w}) \equiv [\exp(\beta\hbar sw)-1]^{-1},\\ \langle n_{\mathbf{k}}\rangle_\beta &= f_e(\mathbf{k}) \equiv [\exp(\alpha+\beta\epsilon_k)+1]^{-1}.\end{aligned}\right\} \quad \ldots\ldots \quad (3.14)$$

The operator $\mathscr{H}_{\mathrm{I}}(\lambda)$ defined by (3.4) is easily obtained from $\mathscr{H}_{\mathrm{I}}$ by the following substitutions

$$\left.\begin{aligned}a_{\mathbf{k}} &\to a_{\mathbf{k}}\exp(-\lambda\epsilon_k), \quad a_{\mathbf{k}}^* \to a_{\mathbf{k}}^*\exp(\lambda\epsilon_k),\\ b_{\mathbf{w}} &\to b_{\mathbf{w}}\exp(-\lambda\hbar sw), \quad b_{\mathbf{w}}^* \to b_{\mathbf{w}}^*\exp(\lambda\hbar sw),\end{aligned}\right\} \quad \ldots \quad (3.15)$$

because then $\mathscr{H}_{\mathrm{I}}(\lambda)$ satisfies

$$\frac{d\mathscr{H}_{\mathrm{I}}(\lambda)}{d\lambda} = -[\mathscr{H}_{\mathrm{I}}(\lambda), \mathscr{H}_0']_-,$$

which is equivalent to (3.4) (with $\mathscr{H}_0'$ instead of $\mathscr{H}_0$).

Since $\mathscr{H}_{\mathrm{I}}$ is non-diagonal with respect to the occupation numbers, the first order correction $\langle\mathscr{H}_{\mathrm{I}}\rangle_\beta$ obviously vanishes. As for the second order correction, $b_{\mathbf{w}}b_{\mathbf{u}}$, $b_{\mathbf{w}}^*b_{\mathbf{u}}^*$ are always non-diagonal, and

$$\langle b_{\mathbf{w}}^*b_{\mathbf{u}}\rangle_\beta = \delta_{\mathbf{w},\mathbf{u}}\, f_p(\mathbf{w}), \quad \langle b_{\mathbf{w}}b_{\mathbf{u}}^*\rangle_\beta = \delta_{\mathbf{w},\mathbf{u}}(1+f_p(\mathbf{w})).$$

where we have made use of (3.11). Similarly

$$\langle a^*_{\mathbf{k}+\mathbf{w}}a_{\mathbf{k}}a^*_{\mathbf{l}-\mathbf{w}}a_{\mathbf{l}}\rangle_\beta = \delta_{\mathbf{l},\mathbf{k}+\mathbf{w}}f_e(\mathbf{k}+\mathbf{w})(1-f_e(\mathbf{k})).$$

Thus

$$\begin{aligned}\epsilon^2\langle\mathscr{H}_{\mathrm{I}}(\lambda)\mathscr{H}_{\mathrm{I}}\rangle_\beta = \Sigma\,|C(\mathbf{w})|^2\{&f_e(\mathbf{k}+\mathbf{w})(1-f_e(\mathbf{k}))\\ &\times(1+f_p(\mathbf{w}))\exp[\lambda(\epsilon_{k+w}-\epsilon_k-\hbar sw)]+f_e(\mathbf{k})(1-f_e(\mathbf{k}+\mathbf{w}))\\ &\times f_p(\mathbf{w})\exp[-\lambda(\epsilon_{k+w}-\epsilon_k-\hbar sw)]\}.\end{aligned}$$

Integrating this over $\lambda$ and using (2.14), we obtain the second order free energy correction due to $\mathscr{H}_{\mathrm{I}}$

$$\begin{aligned}&\Sigma\frac{|C(\mathbf{w})|^2}{\epsilon_{k+w}-\epsilon_k-\hbar sw}\{f_e(\mathbf{k}+\mathbf{w})(1-f_e(\mathbf{k}))(1+f_p(\mathbf{w}))+f_e(\mathbf{k})(1-f_e(\mathbf{k}+\mathbf{w}))f_p(\mathbf{w})\}\\ &\quad=\Sigma'\frac{|C(\mathbf{w})|^2}{\epsilon_{k+w}-\epsilon_k-\hbar sw}f_p(\mathbf{w})(f_e(\mathbf{k}+\mathbf{w})-f_e(\mathbf{k}))\\ &\qquad+\Sigma'\frac{|C(\mathbf{w})|^2}{\epsilon_{k+w}-\epsilon_k-\hbar sw}f_e(\mathbf{k}+\mathbf{w})(1-f_e(\mathbf{k})), \quad \ldots\ldots \quad (3.16)\end{aligned}$$

where $\Sigma'$ indicates taking the principal value at the pole, so that the total sum on the right-hand side reduces to the regular expression on the left-hand side. The first term on the right is the self-energy correction of the phonon. The velocity of sound correction $\delta s$ must therefore be given such a value that this term is cancelled by the first order free energy correction due to $\delta\mathscr{H}$ in (3.13),

$$-\langle\delta\mathscr{H}\rangle_\beta = -\Sigma\hbar w\delta s f_p(\mathbf{w}),$$

because such a self-energy correction has already been taken into account in the unperturbed Hamiltonian $\mathscr{H}_0'$. Thus we require that

$$\hbar w\delta s = |C(\mathbf{w})|^2 \sum_{\mathbf{k}}{}' \frac{f_e(\mathbf{k}+\mathbf{w})-f_e(\mathbf{k})}{\epsilon_{k+w}-\epsilon_k-\hbar sw}. \quad . \quad . \quad . \quad . \quad (3.17)$$

The remaining free energy correction, up to the second order, is then given by

$$\epsilon^2 F_2 = \Sigma' \frac{|C(\mathbf{w})|^2}{\epsilon_{k+w}-\epsilon_k-\hbar sw} f_e(\mathbf{k}+\mathbf{w})(1-f_e(\mathbf{k})). \quad . \quad . \quad . \quad (3.18)$$

It represents the interaction between electrons and holes, which was first studied by Fröhlich (1950), and leads to the modification of the level density near the Fermi surface as shown by Buckingham and Schafroth (1954).

## § 4.

In this section we shall discuss the diamagnetism of a gas composed of charged particles (for instance, the free electrons in metals). From a physical point of view, the problem is very complicated because of its surface effects, and of its non-linear effect at low temperatures (the de Haas–van Alphen effect, the coupling with the spin paramagnetism) etc. (Dingle 1952.) The exact solution has been obtained for an ideal Fermi gas (Sondheimer and Wilson 1951). If, however, we take into account the periodic electric field in metals or the electron–phonon interaction, or the electron–electron Coulomb interaction, it will be practically impossible to get a rigorous solution (cf. Wilson 1953). Furthermore, when the system is known to exhibit the Meissner effect, we can never assume the magnetic field to be uniform as is done in the usual procedure. A very simple example of such a system is the charged ideal Bose gas, which shows the Meissner effect below its Bose condensation temperature (Schafroth 1954). It is not intended to enter into such physical details of this model; the reason for our choice is that the example is formally simple for the purpose of comparing our statistical perturbation theory with that of quantum mechanics.

Consider thus the system of $N$ similar particles, each having the mass $m$ and the charge $e$. We treat the system as a quantized wave field described by the variable $\psi(\mathbf{x})$ and its conjugate $\psi^*(\mathbf{x})$, which satisfy the well-known commutation or anti-commutation relations

$$[\psi(\mathbf{x}), \quad \psi^*(\mathbf{x}')]_{\pm} = \delta(\mathbf{x}-\mathbf{x}').$$

Whenever the double signs occur, the upper sign refers to Fermi statistics and the lower to Bose statistics. We adopt the Schafroth method for diamagnetism, whose physical aspects will be discussed in § 5. In this method, we suppose the system to be enclosed in a very large volume $V$ and impose the cyclic boundary condition. Therefore field variables are Fourier-developed like

$$\psi(\mathbf{x}) = V^{-1/2}\Sigma a_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{x}), \quad \psi^*(\mathbf{x}) = V^{-1/2}\Sigma a_{\mathbf{k}}^* \exp(-i\mathbf{k}\cdot\mathbf{x}), \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

where $a_{\mathbf{k}}$, $a_{\mathbf{k}}^*$ respectively are destruction and creation operators of the particle with the wave vector $\mathbf{k}$.

We assume that the mutual Coulomb repulsion between particles is nearly cancelled by a suitable static charge of opposite sign, and neglect it. Then the unperturbed Hamiltonian is given by

$$\mathscr{H}_0=\Sigma\epsilon_k n_{\mathbf{k}}, \quad \epsilon_k=\frac{\hbar^2}{2m}k^2,$$

where $n_{\mathbf{k}}=a_{\mathbf{k}}^*a_{\mathbf{k}}$ is the occupation number, whose expectation value is given by

$$\langle n_{\mathbf{k}}\rangle_\beta=f(\mathbf{k})\equiv[\exp(\alpha+\beta\epsilon_k)\pm1]^{-1}. \quad . \quad . \quad . \quad . \quad (4.2)$$

Now in order to establish a finite magnetic field in the very large system, we put the external current density $\mathbf{J}_e$ inside the system. $\mathbf{J}_e$ produces the external magnetic field $\mathbf{H}_e$ which induces the current density $\mathbf{J}$ and the associated magnetic field $\mathbf{H}_i$ in the system. As is well-known, the total field $\mathbf{H}_i+\mathbf{H}_e$ should be identified not with the macroscopic magnetic field $\mathbf{H}$, but with the magnetic induction $\mathbf{B}$, which can be expressed as

$$\mathbf{B}=\text{curl }\mathbf{A}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.3)$$

We assume that each particle is moving in the field $\mathbf{B}$: this means a sort of Hartree approximation with respect to the magnetic interaction and will be justified in § 5, and in the Appendix. Then the perturbation due to the magnetic field is given by

$$\epsilon\mathscr{H}_{\mathrm{I}}=-\frac{1}{c}\int\mathbf{A}(\mathbf{x})\cdot\mathbf{j}_p(\mathbf{x})\,d\mathbf{x}-\frac{1}{2c}\int\mathbf{A}(\mathbf{x})\cdot\mathbf{j}_d(\mathbf{x})\,d\mathbf{x}. \quad . \quad . \quad (4.4)$$

where

$$\mathbf{j}_p=\frac{\hbar e}{2mi}(\psi^*\nabla\psi-\text{c.c.}), \quad \mathbf{j}_d=-\frac{e^2}{mc}\psi^*\psi\mathbf{A} \quad . \quad . \quad . \quad (4.5)$$

are the paramagnetic and the diamagnetic parts of the current density $\mathbf{j}$, respectively. The Hamiltonian is a functional of the vector potential $\mathbf{A}(\mathbf{x})$ and its functional derivative is

$$\frac{\delta\mathscr{H}}{\delta A\mu(\mathbf{x})}=-\frac{1}{c}j_\mu(\mathbf{x}), \quad \mu=x, y, z.$$

In much the same way as in the case of (3.6), it can be shown that the average current density is given by

$$J_\mu(\mathbf{x})\equiv\mathrm{Tr}[\exp(-\beta\mathscr{H})j_\mu(\mathbf{x})]/\mathrm{Tr}[\exp(-\beta\mathscr{H})]=-c\frac{\delta F}{\delta A\mu(\mathbf{x})}, \quad . \quad (4.6)$$

where $F$ is the free energy.

The free energy will now be calculated up to the second order of the vector potential by means of perturbative theory. By inserting Fourier transforms

$$\psi^*\psi=V^{-1}\Sigma a_{\mathbf{l}}^*a_{\mathbf{l}+\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{x}),$$

$$\frac{1}{i}(\psi^*\nabla\psi-\text{c.c.})=V^{-1}\Sigma(2\mathbf{l}+\mathbf{k})a_{\mathbf{l}}^*a_{\mathbf{l}+\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{x})$$

into (4.4) and using the same technique as in § 3, it is easily found that

$$\epsilon\langle \mathscr{H}_{\mathrm{I}}\rangle_\beta = \frac{e^2}{2mc^2}\int d\mathbf{x}A^2(\mathbf{x})\,\frac{1}{V}\sum_{\mathbf{l}} f(\mathbf{l}),$$

and

$$\epsilon^2\langle \mathscr{H}_{\mathrm{I}}(\lambda)\,\mathscr{H}_{\mathrm{I}}\rangle_\beta = \left(\frac{\hbar e}{2mcV}\right)^2 \Sigma \int\!\!\int d\mathbf{x}\, d\mathbf{x}'A_\mu(\mathbf{x})A_\nu(\mathbf{x}')$$
$$\times \exp\,[i(\mathbf{p}-\mathbf{q})\,.\,(\mathbf{x}-\mathbf{x}')](p_\mu+q_\mu)(p_\nu+q_\nu)\exp\,[\lambda(\epsilon_q-\epsilon_p)]\,f(\mathbf{q})(1\mp f(\mathbf{p})).$$

Integrating this over $\lambda$, leads to the factor

$$f(\mathbf{q})(1\mp f(\mathbf{p}))(\exp\,(\epsilon_q-\epsilon_p)-1)/(\epsilon_q-\epsilon_p) = -(f(\mathbf{p})-f(\mathbf{q}))/(\epsilon_p-\epsilon_q).$$

Thus the free energy is given by

$$F = F_0 + \frac{e^2}{2mc^2}\,\frac{N}{V}\int d\mathbf{x}A^2(\mathbf{x}) + \frac{1}{2}\left(\frac{\hbar e}{2mcV}\right)^2\int\!\!\int d\mathbf{x}\,d\mathbf{x}'A_\mu(\mathbf{x})A_\nu(\mathbf{x}')$$
$$\times \sum_{\mathbf{p},\,\mathbf{q}}\exp\,[i(\mathbf{p}-\mathbf{q})\,.\,(\mathbf{x}-\mathbf{x}')](p_\mu+q_\mu)(p_\nu+q_\nu)(f(\mathbf{p})-f(\mathbf{q}))/(\epsilon_p-\epsilon_q). \qquad (4.7)$$

Therefore, by (4.6), the average induced current can be expressed in the form

$$J_\mu(\mathbf{x}) = \Sigma\int K_{\mu\nu}(\mathbf{x}-\mathbf{x}')A_\nu(\mathbf{x}')\,d\mathbf{x}', \quad . \quad . \quad . \quad . \quad (4.8)$$

where the Fourier transform of the kernel $K_{\mu\nu}$ takes the simple form

$$K_{\mu\nu}(\mathbf{k}) \equiv \int K_{\mu\nu}(\mathbf{x})\exp\,(-i\mathbf{k}\,.\,\mathbf{x})\,d\mathbf{x}$$
$$= -\frac{e^2}{mcV}\,\delta_{\mu\nu}\sum_{\mathbf{q}} f(\mathbf{q}) - \frac{\hbar^2e^2}{m^2cV}\sum_{\mathbf{q}} q_\nu\left(q_\mu+\frac{1}{2}k_\mu\right)$$
$$\times (f(\mathbf{q}+\mathbf{k})-f(\mathbf{q}))/(\epsilon_{k+q}-\epsilon_q). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.9)$$

This formula was first derived by Schafroth (1951).

For the simple case of a Bose gas at the absolute zero ($\beta=\infty$), where the distribution function is a singular function

$$f(\mathbf{q}) = \begin{cases} N & \mathbf{q}=0 \\ 0 & \mathbf{q}\neq 0, \end{cases}$$

equation (4.9) gives

$$K_{\mu\nu}(\mathbf{k}) = (k^2\delta_{\mu\nu}-k_\mu k_\nu)K(k^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.10)$$

with

$$K(k^2) = -\frac{e^2}{mc}\,\frac{N}{V}\cdot\frac{1}{k^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.11)$$

Returning to $\mathbf{x}$-space, (4.8) gives the London equation

$$\operatorname{curl}\mathbf{J} = -\frac{e^2}{mc}\,\frac{N}{V}\,\mathbf{B}.$$

At finite temperatures below the Bose condensation temperature, $f(\mathbf{q})$ is still singular and the physical result will remain unaltered (for details see Schafroth 1954).

On the other hand, if $f(\mathbf{q})$ is regular, we can never obtain the Meissner effect. In this case we expand

$$\frac{f(\mathbf{q}+\mathbf{k})-f(\mathbf{q})}{\epsilon_{q+k}-\epsilon_q}=\frac{\partial f}{\partial \epsilon_q}+\frac{1}{2}(\epsilon_{q+k}-\epsilon_q)\frac{\partial^2 f}{\partial {\epsilon_q}^2}+\cdots.$$

The contribution of the first term to (4.9) is, by partial integration, exactly cancelled by the first term of (4.9), and therefore (4.9) begins with the term proportional to $k^2$. As we shall see in § 5, this leads to the normal diamagnetism. In fact, Schafroth (1951) obtained the Landau diamagnetism for the Fermi gas in this way.

It is possible to take account of the periodic electric field produced by lattice ions in metals by expanding $\psi$, $\psi^*$ in terms of the Bloch eigenfunctions instead of the plane waves as in (4.1). But the actual evaluation of various integrals seems hopeless at the present stage of our knowledge of the wave function for metallic electrons. Our method will be useful, however, in cases where account is taken of the electron–photon interaction or of the electron–electron Coulomb interaction (i.e. the plasma oscillation in the stationary magnetic field).

Now, in order to compare the above theory with quantum mechanical perturbation theory, the latter will be used to treat the same charged gas at absolute zero. In quantum mechanics, the state vector $\Phi(t)$ obeys the time-dependent Schrödinger equation

$$i\hbar\,\Phi\,(t)=(\mathscr{H}_0+\epsilon\mathscr{H}_{\mathrm{I}})\,\Phi(t).$$

The transformation

$$\Phi(t)=\exp\left(-\frac{i}{\hbar}t\,\mathscr{H}_0\right)\Psi(t)$$

leads to the so-called interaction representation

$$i\hbar\,\Psi(t)=\epsilon\,\mathscr{H}_{\mathrm{I}}(t)\,\Psi(t), \qquad (4.12)$$

where

$$\mathscr{H}_{\mathrm{I}}(t)=\exp\left(\frac{i}{\hbar}t\,\mathscr{H}_0\right)\mathscr{H}_{\mathrm{I}}\exp\left(-\frac{i}{\hbar}t\,\mathscr{H}_0\right). \qquad (4.13)$$

Let $\Phi_0$ be the eigenfunction which belongs to the lowest energy level of $\mathscr{H}_0$. We suppose that at the remote past $t=-\infty$ the system was found in the state $\Phi_0$ without magnetic field, the latter being then switched on adiabatically. The approximate solution of (4.12) is given by

$$\Psi(t)\simeq\left(1-\frac{i}{\hbar}\int_{-\infty}^{t}\epsilon\,\mathscr{H}_{\mathrm{I}}(t')\,dt'\right)\Phi_0. \qquad (4.14)$$

The expectation value of the current density $\mathbf{j}$ at the time $t$ is given by

$$\begin{aligned}J_\mu(\mathbf{x},t)&\equiv\langle\Phi(t),j_\mu(\mathbf{x})\,\Phi(t)\rangle\\&=\langle\Psi(t),j_\mu(\mathbf{x},t)\,\Psi(t)\rangle,\end{aligned} \qquad (4.15)$$

where

$$j_\mu(\mathbf{x},t)=\exp\left(\frac{i}{\hbar}t\,\mathscr{H}_0\right)j_\mu(\mathbf{x})\exp\left(-\frac{i}{\hbar}t\,\mathscr{H}_0\right). \qquad (4.16)$$

The time-dependent operators (4.13), (4.16) are easily obtained from the corresponding time-independent operators by the substitutions

$$a_{\mathbf{k}} \to a_{\mathbf{k}} \exp\left(\frac{-i}{\hbar}\epsilon_k t\right), \quad a_k{}^* \to a_k{}^* \exp\left(\frac{i}{\hbar}\epsilon_k t\right).$$

Inserting (4.14) into (4.15), we have

$$J_\mu(\mathbf{x}, t) = \langle j_\mu(\mathbf{x}, t)\rangle_0 + \frac{i}{\hbar}\int_{-\infty}^{t} dt' \langle [\epsilon \mathscr{H}_{\mathrm{I}}(t'), j_\mu(\mathbf{x}, t]_-\rangle_0,$$

where $\langle \ldots \rangle_0$ is the expectation value with respect to the state $\Phi_0$. Its evaluation can be carried out in much the same way as that of $\langle \ldots \rangle_\beta$. The result can be expressed as

$$J_\mu(\mathbf{x}, t) = -\frac{e^2}{mc}\frac{N}{V}A_\mu(\mathbf{x}) + \frac{1}{c}\left(\frac{\hbar e}{2mV}\right)^2 \int d\mathbf{x}' A_\nu(\mathbf{x}')$$
$$\times \sum_{\mathbf{p},\mathbf{q}} \exp\left[i\,(\mathbf{p}-\mathbf{q})\cdot(\mathbf{x}-\mathbf{x}')\right](p_\mu+q_\mu)(p_\nu+q_\nu)(n_p{}^0-n_q{}^0)$$
$$\times \frac{i}{\hbar}\int_{-\infty}^{t} dt' \exp\left(-\frac{i}{\hbar}(\epsilon_p-\epsilon_q)(t-t')\right),$$

where $n_q{}^0$ is the occupation number in the state $\Phi_0$, so that it equals $f(\mathbf{q})$ at $\beta = \infty$. The time integral is transcribed as

$$i\int_{-\infty}^{0} d\tau \exp\left[-i(\epsilon_p-\epsilon_q)\tau\right] = \frac{-\mathfrak{P}}{\epsilon_p-\epsilon_q} + i\pi\delta\,(\epsilon_p-\epsilon_q),$$

where $\mathfrak{P}$ means taking the principal value where the energy denominator vanishes (Heitler 1954). The $\delta$-function part, which corresponds to the real transition, does not make any contribution to $J_\mu$, because it appears there with the factor $(n_p{}^0-n_q{}^0)$ which vanishes for $\epsilon_q=\epsilon_p$. Thus our previous result is formally valid even at $\beta=\infty$, provided that the principal value is to be taken at vanishing energy denominators.

## § 5.

Finally we shall give a brief account of Schafroth's general method of dealing with problems of diamagnetism, including the Meissner effect. In his method, as has been seen, we consider a practically infinite system. This means that macroscopic boundary conditions do not occur. At the same time, however, surface effects which experimentally are very hard to separate from the internal properties cannot be taken into account.

Assume an external current density $\mathbf{J}_e$ which may have any spacial distribution. For instance, we may suppose a circuit of finite intensity to be concentrated at a point. Then in ordinary diamagnetic substances, the field will be proportional to $r^{-1}$, where $r$ is the distance from the point circuit. In superconductors, however, the external field $\mathbf{H}_e$ produced by $\mathbf{J}_e$ is nearly shielded by the induced current and the actual field will be proportional to $\exp(-r/\lambda)/r$ where $\lambda$ is a constant called the penetration depth.

Now we express the magnetic fields in terms of the external and internal vector potentials $\mathbf{A}_e$ and $\mathbf{A}_i$,

$$\mathbf{H}_e = \mathrm{curl}\,\mathbf{A}_e, \quad \mathbf{H}_i = \mathrm{curl}\,\mathbf{A}_i. \qquad \ldots\ldots \quad (5.1)$$

We shall adopt the Coulomb gauge of the vector potential, so that

$$\mathrm{div}\,\mathbf{A}_e = 0, \qquad \nabla^2\mathbf{A}_e = -\frac{4\pi}{c}\mathbf{J}_e. \qquad \ldots \quad (5.2)$$

We regard $\mathbf{A}_e$ as a simple external potential. As for $\mathbf{A}_i$, however, account must be taken of the magnetic interaction between particles. For this purpose introduce orthogonal real vectors $\mathbf{A}_0(\mathbf{x})$ which satisfy

$$\mathrm{div}\,\mathbf{A}_\lambda = 0, \qquad \nabla^2\mathbf{A}_\lambda + \frac{{\nu_\lambda}^2}{c^2}\mathbf{A}_\lambda = 0, \qquad \int \mathbf{A}_\lambda \,.\, \mathbf{A}_\mu \, d\mathbf{x} = 4\pi c^2\,\delta_{\lambda\mu},$$

and make the expansion

$$\mathbf{A}_i(\mathbf{x}) = \sum_\lambda q_\lambda\,\mathbf{A}_\lambda(\mathbf{x}).$$

According to Heitler (1954), the total Hamiltonian is given by

$$\mathscr{H}_{\mathrm{tot}} = \mathscr{H}_p + \mathscr{H}_f + \epsilon\,\mathscr{H}_{\mathrm{I}},$$

where

$$\mathscr{H}_p = \int d\mathbf{x}\,\psi^*\left(-\frac{\hbar^2}{2m}\nabla^2\right)\psi + \phi,$$

$$\mathscr{H}_f = \sum_\lambda \frac{1}{2}({p_\lambda}^2 + {\nu_\lambda}^2 {q_\lambda}^2),$$

and $\epsilon\,\mathscr{H}_{\mathrm{I}}$ is given by (4.4). $\phi$ is the interparticle potential including the electrostatic Coulomb interaction, and $p_\lambda$ is the momentum conjugate to $q_\lambda$. The vector potential $\mathbf{A}$ appearing in $\epsilon\,\mathscr{H}_{\mathrm{I}}$ is given by

$$\mathbf{A} = \mathbf{A}_i + \mathbf{A}_e. \qquad \ldots\ldots\ldots\ldots \quad (5.3)$$

For our purpose it is sufficient to treat the induced field $\mathbf{H}_i$ as a macroscopic field, so that the vector potential $\mathbf{A}$ leads to the macroscopic induction $\mathbf{B}$ given by (4.3). This means that we neglect all (quantum mechanical as well as statistical) fluctuations of the field variables $q_\lambda$, $p_\lambda$ In other words, $q_\lambda$, $q_\lambda$ are regarded not as dynamical variables, but as quasi-static parameters, which should be determined so as to minimize the free energy.

The variation of the free energy is given by

$$\exp(-\beta F_{\mathrm{tot}})\,\delta F_{\mathrm{tot}} = \mathrm{Tr}\,(\exp[-\beta\,\mathscr{H}_{\mathrm{tot}}]\,\delta\mathscr{H}_{\mathrm{tot}}),$$

where

$$\delta\mathscr{H}_{\mathrm{tot}} = \Sigma p_\lambda\,\delta p_\lambda + \Sigma\delta q_\lambda\left({\nu_\lambda}^2 q_\lambda - \frac{1}{c}\int \mathbf{j}\,.\,\mathbf{A}_\lambda\,d\mathbf{x}\right).$$

Thus $\delta F_{\mathrm{tot}} = 0$ leads to

$$p_\lambda = 0, \quad {\nu_\lambda}^2\, q_\lambda = \frac{1}{c}\int \mathbf{J}\,.\,\mathbf{A}_\lambda\,d\mathbf{x}, \qquad \ldots\ldots\ldots \quad (5.4)$$

where

$$\mathbf{J}(\mathbf{x}) \equiv \exp(\beta F_{\mathrm{tot}})\,\mathrm{Tr}\,(\exp[-\beta\,\mathscr{H}_{\mathrm{tot}}]\,\mathbf{j}(\mathbf{x}))$$
$$= \mathrm{Tr}\,\{\exp[-\beta(\mathscr{H}_p + \epsilon\,\mathscr{H}_{\mathrm{I}})]\,\mathbf{j}(\mathbf{x})\}/\mathrm{Tr}\,\{\exp[-\beta(\mathscr{H}_p + \epsilon\,\mathscr{H}_{\mathrm{I}})]\}. \qquad \ldots \quad (5.5)$$

Equation (5.4) is equivalent to the ampere law

$$\operatorname{div} \mathbf{A}_i=0, \quad \nabla^2\mathbf{A}_i=\frac{-4\pi}{c}\mathbf{J}, \quad \ldots \ldots \quad (5.6)$$

and the expression (5.5) for the average induced current agrees with (4.6).

Now, using perturbation theory to evaluate (5.5), the result can always be written in the form (4.8), as far as the non-linear effect is neglected. The Fourier transform of the integral kernel $K_{\mu\nu}$ generally has the form (4.10), since **J** must satisfy the continuity equation and the requirement of gauge invariance.

Now the normal diamagnetic system is characterized by the condition that $K(k^2)$ in (4.10) is regular at $k=0$:

$$K(k^2)=K_r(k^2)=\gamma+\gamma_1 k^2+\ldots .$$

Then, going back to **x**-space, we have

$$\mathbf{J}(\mathbf{x})=\operatorname{curl}(\gamma\mathbf{B}(\mathbf{x})-\gamma_1\nabla^2\mathbf{B}(\mathbf{x})+\ldots). \quad \ldots \ldots \quad (5.7)$$

Therefore, (5.2) and (5.6) are combined to

$$\operatorname{curl}\left(\left(1-\frac{4\pi}{c}\gamma\right)\mathbf{B}(\mathbf{x})+\gamma_1\nabla^2\mathbf{B}(\mathbf{x})+\ldots\right)=\frac{4\pi}{c}\mathbf{J}_e(\mathbf{x}). \quad \ldots \ldots \quad (5.8)$$

Usually the diamagnetic property is expressed in terms of the susceptibility $\chi$. Taking the limit of the uniform field in (5.8) ($k \to 0$ in **k**-space) and comparing it with the phenomenological ampere law, we obtain

$$\chi=\frac{\gamma}{c}\frac{1}{1-4\pi\gamma/c}. \quad \ldots \ldots \quad (5.9)$$

It should be noted that the conventional method of deriving the Landau diamagnetism, for instance, gives $\gamma/c$ instead of $\chi$. Usually $|\chi| \ll 1$, so that $\chi \simeq \gamma/c$. But this is no longer true for large $|\gamma|$, and always $|\chi|<1/4\pi$. (Perfect diamagnetism corresponds to $\gamma=-\infty$.) Attempts have often been made to find the Meissner effect by showing that the Landau diamagnetism becomes very large, because of the small effective mass of the electron, for instance. Obviously such an attempt is mistaken as was pointed out first by Fröhlich (1951), who derived (5.9) by considering the macroscopic boundary conditions.

The Meissner effect is characterized not by a large $\gamma$, but by a *mathematical singularity* of $K(k^2)$. Suppose $K(k^2)$ has a pole at $k=0$:

$$K(k^2)=\frac{\alpha}{k^2}+K_r(k^2). \quad \ldots \ldots \quad (5.10)$$

Correspondingly we divide **J** into two parts

$$\mathbf{J}=\mathbf{J}_s+\mathbf{J}_r,$$

where $\mathbf{J}_r$ is the part arising from the regular kernel $K_r$ and therefore can be treated in the same way as before, whereas $\mathbf{J}_s$ arises from the singular part of the kernel. We can no longer take the limit $k \to 0$ for this part but we must treat it as a macroscopic current in addition to the external current $\mathbf{J}_e$; thus, instead of (5.8), we have

$$\operatorname{curl}\left(\left(1-\frac{4\pi}{c}\gamma\right)\mathbf{B}+\gamma_1\nabla^2\mathbf{B}+\ldots\right)=\frac{4\pi}{c}(\mathbf{J}_e+\mathbf{J}_s), \quad \ldots \quad (5.11)$$

where $\mathbf{J}_s$ obeys the London equation

$$\operatorname{curl} \mathbf{J}_s = \alpha \mathbf{B}. \qquad (5.12)$$

These equations, apart from the field inhomogeneity correction, agree with those assumed by London in his phenomenological theory of superconductivity. In this case the ordinary diamagnetism arising from the regular part of the induced current can be neglected, so that

$$(-\nabla^2+\lambda^{-2})\mathbf{B} = \frac{4\pi}{c} \operatorname{curl} \mathbf{J}_e, \qquad \lambda^{-2} = -\frac{4\pi\alpha}{c}.$$

Remembering that $\mathbf{J}_e$ satisfies the continuity equation, we can easily deduce the Fourier transform of the vector potential in the Coulomb gauge

$$\mathbf{A}(\mathbf{k}) = \frac{4\pi}{c} \frac{\mathbf{J}_e(\mathbf{k})}{k^2+\lambda^{-2}},$$

which can be as small as desired for *all* $\mathbf{k}$ by suitable choice of external current, so that the application of perturbation theory is guaranteed. For normal diamagnetics, however, we have $\lambda \to 0$, so that first we exclude the uniform part $\mathbf{k}=0$ and take the limit $\mathbf{k} \to 0$ afterwards.

## ACKNOWLEDGMENTS

I wish to express my thanks to Professor Fröhlich for his encouragement and illuminating discussions. I am also indebted to the British Council for the award of a Scholarship.

---

## APPENDIX

### *The Hartree Method*

The Hartree Method in statistical mechanics is based on the fact that the density operator $R = \exp(-\beta\mathscr{H})$ is specified by the variation principle: the entropy defined by

$$S = -\operatorname{Tr}(R \log R) \qquad (A.1)$$

should be maximum under the subsidiary conditions

$$\operatorname{Tr}(R)=1, \quad \operatorname{Tr}(\mathscr{H}R)=E=\text{const.} \qquad (A.2)$$

The Hartree method means to solve this variation problem by neglecting the statistical correlation between subsystems. For simplicity, we suppose the system to be composed of two interacting subsystems:

$$\mathscr{H} = \mathscr{H}_1(q_1) + \mathscr{H}_2(q_2) + \mathscr{H}_I(q_1, q_2). \qquad (A.3)$$

Then, in the Hartree method, we assume that $R$ is given in the form of the direct product,

$$R = R_1(q_1) \times R_2(q_2)$$

with

$$\operatorname{Tr}(R_1)=1, \quad \operatorname{Tr}(R_2)=1.$$

The entropy (A.1) is given by

$$S = -\operatorname{Tr}(R_1 \log R_1) - \operatorname{Tr}(R_2 \log R_2).$$

which is physically obvious and can be verified by taking the representation in which $R_1$ and $R_2$ are diagonalized. The variation of the average energy is given by

$$\delta E = \mathrm{Tr}\,(K_1(q_1)\,\delta R_1) + \mathrm{Tr}\,(K_2(q_2)\,\delta R_2),$$

where

$$K_1\,(q_1) = \mathscr{H}_1\,(q_1) + \mathrm{Tr}\,(\,\mathscr{H}_{\mathrm{I}}\,(q_1, q_2)\,R_2),$$
$$K_2\,(q_2) = \mathscr{H}_2\,(q_2) + \mathrm{Tr}\,(\,\mathscr{H}_{\mathrm{I}}\,(q_1, q_2)\,R_1) \quad . \quad . \quad . \quad . \quad \text{(A.4)}$$

are Hartree fields ; the solution of the variation problem is then given by

$$R_1 = \exp\,(-\beta K_1)/\mathrm{Tr}\,[\exp\,(-\beta K_1)], \;\; R_2 = \exp\,(-\beta K_2)/\mathrm{Tr}\,[\exp\,(-\beta K_2)]$$
$$. \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(A.5)}$$

We shall apply this method to the system of charged particles in a magnetic field (§ 5). We neglect the correlation between the particle system and the field. Then the Hartree field for the magnetic field is given by

$$K_f = \mathscr{H}_f - \frac{1}{c}\,\Sigma\,q_\lambda \int d\mathbf{x}\,\mathbf{A}_\lambda\,.\,\mathrm{Tr}\,(\mathbf{j}_p\,R_p)$$
$$- \frac{e^2}{2mc^2}\,\Sigma\,q_\lambda\,q_\mu \int d\mathbf{x}\,\mathbf{A}_\lambda\,.\,\mathbf{A}_\mu\,\mathrm{Tr}\,(\psi^*\psi\,R_p),$$

where $R_p$ is the density operator for the particle system. We may take $\mathrm{Tr}\,(\psi^*\psi\,R_p)$ to be equal to the average density $\rho_0$, in so far as surface effects are neglected. Then the canonical equations for the field variables give

$$\ddot{q}_\lambda + (\nu_\lambda{}^2 + \nu_p{}^2)\,q_\lambda = \frac{1}{c}\int d\mathbf{x}\,\mathbf{A}_\lambda\,.\,\mathrm{Tr}\,(\mathbf{j}_p\,R_p), \quad . \quad . \quad . \quad \text{(A.6)}$$

where

$$\nu_p{}^2 = \frac{4\pi e^2 \rho_0}{m}$$

is the well-known plasma frequency.

The solution of (A.6) takes the form

$$q_\lambda = q_\lambda{}' + Q_\lambda,$$

where

$$q_\lambda{}' + (\nu_\lambda{}^2 + \nu_p{}^2)q_\lambda{}' = 0,$$
$$(\nu_\lambda{}^2 + \nu_p{}^2)\,Q_\lambda = \frac{1}{c}\int d\mathbf{x}\,\mathbf{A}_\lambda\,.\,\mathrm{Tr}\,(\mathbf{j}_p R_p)\,.$$

The equation for $Q_\lambda$ is equivalent to the macroscopic ampere law (5.4). Since the plasma frequency is very high ($10^{15}$ sec$^{-1}$ for metals), the quantum mechanical and statistical fluctuations of the field can be neglected :

$$\mathrm{Tr}\,(q_\lambda\,R_f) = Q_\lambda, \;\; \mathrm{Tr}\,(q_\lambda{}^2\,R_f) \cong Q_\lambda{}^2 + \frac{\hbar}{2\sqrt{(\nu_\lambda{}^2 + \nu_p{}^2)}},$$

where $R_f$ is the density operator for the magnetic field. Therefore, the Hartree field for the particle system becomes

$$K_p = \mathscr{H}_p - \frac{1}{c}\int \mathbf{A}_c\,.\,\mathbf{j}_p\,d\mathbf{x} - \frac{e^2}{2mc^2}\int A_c{}^2\,\psi^*\psi\,d\mathbf{x},$$

where

$$\mathbf{A}_c = \sum_{\lambda} Q_\lambda \, \mathbf{A}_\lambda(\mathbf{x})$$

is the macroscopic vector potential. Thus (5.5) is again justified.

*Note added in proof.*—Recently Matsubara (to be published in *Prog. Theor. Phys.*) has developed a systematic method of evaluating the expectation values mentioned in paragraph 3. The method is very similar to the graphic technique of Feynman and Dyson in quantum field theory.

Perturbation theory can also be extended to include relaxation phenomena. Thus Kubo and Tomita (1954, *J. Phys. Soc., Japan*, **9,** 888) have treated magnetic resonance absorption and Nakano (1955, *Busseiron Kenkyu*, **84,** 25) has applied the same method to electric conductivity of metals.

## References

Buckingham, M. J., and Schafroth, M. R., 1954, *Proc. Phys. Soc.* A, **67,** 828.
Dingle, R. D., 1952, *Proc. Roy. Soc.* A, **211,** 500.
Dyson, F. J., 1949, *Phys. Rev.*, **75,** 486.
Fröhlich, H., 1950, *Phys. Rev.*, **79,** 845; 1951, *Nature, Lond.*, **168,** 280; 1953, *Proc. Roy. Soc.* A, **223,** 296.
Gell-Mann, M., and Goldberger, M. L., 1953, *Phys. Rev.*, **91,** 398.
Goldberger, M. L., and Adams, E. N., 1952, *J. Chem. Phys.*, **20,** 240.
Heitler, W., 1954, *Quantum Theory of Radiation*, 3rd Edition (Oxford: Clarendon Press).
Hushimi, K., 1940, *Proc. Phys. Math. Soc. Japan*, **22,** 264.
Kubo, R., 1952, *J. Chem. Phys.*, **20,** 770.
Peierls, R. E., 1932, *Z. Phys.*, **80,** 763.
Schafroth, M. R., 1951, *Helv. Phys. Acta*, **24,** 645; 1954, *Phys. Rev.*, **96,** 1154.
Sondheimer, E. H., and Wilson, A. H., 1951, *Proc. Roy. Soc.* A, **210,** 173.
van Vleck, J. H., 1932, *The Theory of Electric and Magnetic Susceptibilities* (Oxford: Clarendon Press).
Wigner, E. P., 1932, *Phys. Rev.*, **40,** 749.
Wilson, A. H., 1953, *Proc. Camb. Phil. Soc.*, **5,** 89.

# *A Survey of Irradiation Effects in Metals*

By J. W. Glen
The Royal Society Mond Laboratory, Cambridge*

## CONTENTS

PART I. GENERAL CONCEPTS

§ 1. INTRODUCTION.
§ 2. NATURE OF RADIATION DAMAGE.
§ 3. THEORY OF RADIATION DAMAGE.
§ 4. ANNEALING OF RADIATION DAMAGE.

PART II. EXPERIMENTAL MEASUREMENTS OF IRRADIATION EFFECTS

§ 5. RADIATION EFFECTS ON THE ELECTRICAL RESISTANCE OF PURE METALS.
§ 6. RADIATION EFFECTS ON THE ELECTRICAL RESISTANCE OF ALLOYS.
§ 7. ANNEALING OF THE EXTRA RESISTANCE CAUSED BY IRRADIATION.
§ 8. RADIATION EFFECTS ON THE MECHANICAL PROPERTIES OF METALS.
    8.1. Creep.
    8.2. Hardness.
    8.3. Stress–strain curve : single crystals.
    8.4. Stress–strain curve : polycrystals.
    8.5. Internal friction.
    8.6. Elastic constants.
§ 9. RADIATION INDUCED PHASE CHANGES.
§ 10. RADIATION EFFECTS ON X-RAY DIFFRACTION AND DENSITY.
§ 11. OTHER EFFECTS IN METALS.
    11.1 Diffusion.
    11.2. Thermoelectric effect.
§ 12. RADIATION EFFECTS ON THE PROPERTIES OF SEMICONDUCTORS.
    12.1. Electrical effects.
    12.2. Other effects in semiconductors.
§ 13. ANALOGOUS RADIATION EFFECTS IN NON-METALS.
    13.1. Introduction.
    13.2. Mechanical properties.
    13.3. X-ray, electron and neutron diffraction and density.
    13.4. Diffusion and electrical conductivity.
    13.5. Thermal conductivity.
    13.6. Magnetic susceptibility.
    13.7. Optical effects.
§ 14. SUMMARY.
    14.1. Nature of the damage.
    14.2. Energy needed to produce the damage.
    14.3. Amount of damage.
    14.4. Annealing of the damage.
ACKNOWLEDGMENTS.
REFERENCES.

---

* Formerly at Metallurgy Division, Atomic Energy Research Establishment, Harwell, Berks.

# PART I. GENERAL CONCEPTS

## § 1. INTRODUCTION

THE theory of the scattering of the particles emitted in radioactive decay was worked out very early in the history of nuclear physics. Indeed it was the success of the Rutherford scattering formula that led to the adoption of the nuclear hypothesis; the only way to explain the number of particles scattered through angles larger than a right angle was to suppose that these particles had been deflected by a small concentrated positive charge of radius very much less than that of the atom, which nevertheless had most of the mass of the atom. This centre was called the nucleus, and the success of the resulting picture of atomic structure is demonstrated by the greatly increased understanding of physical and chemical processes to which it led. Most of the experiments by which information about nuclei is obtained are performed by studying the radiation which emerges when a beam of known particles is fired into the substance whose nucleus is being studied, i.e. by measurements of the scattering, absorption and emission of particles. In most of the early experiments attention was focused on the information which scattering gave about the particles or nuclei concerned, and the damage which such scattering caused to the structure of the bulk material was rarely studied. Exceptions were work on the theory of the sputtering of atoms from surfaces, the metamict state of minerals and the coloration of alkali halides. More recently, advances in the design of accelerators and the development of the chain-reacting pile have made available strong sources of radiation, and with these sources it became reasonable to expect large effects on the bulk properties of materials after bombardment for a reasonably short time; and it also became imperative to study these effects in order to predict the behaviour of the structural components of reactors. The purpose of this article is to review the progress which has been made towards a full knowledge of the effects of radiation on the physical properties of solids, and particularly of metals.

To limit the field of this review, no discussion will be given of chemical changes produced by irradiation, such as the production of hydrogen peroxide in ice or the cross-linking of polymers; attention will be given only to those changes which seem to be caused by disrupting the lattice of a solid without changing the nature of the molecules of which it is composed. Because of the incomplete state of the subject, it is not possible to give a satisfactory theoretical account of the damage, but some remarks on the type of effects to be expected will be presented first, and the observed effects will then be discussed.

Previous review articles on the general subject of radiation effects in solids have been written by Slater (1951), Dienes (1953 a) and Kinchin and Pease (1955 b), while shorter surveys have come from Leeser (1952, 1954), Seitz (1952), Koehler and Seitz (1954, 1955), Calkins (1954 a, b) and, in Italian, Mongini (1953). The effects of nuclear radiations on the mechanical properties of solids were reviewed by Dienes (1953 b). On allied topics the review article by Otley (1952) on the effect of radiation on glasses, that of Broom (1954) on the effects of lattice defects (including those caused by radiation) on the electrical resistivity of metals, and the book by Przibram (1953) on the coloration and luminescence of minerals, should also be mentioned.

## § 2. NATURE OF RADIATION DAMAGE

The detailed damage which is produced on irradiation will depend both on the nature of the bombarded material (metal, semiconductor, ionic or covalent solid) and on the nature and energy of the bombarding particle (heavy ion, alpha particle, proton, electron, neutron, x-ray etc.). Nevertheless some general ideas can be proposed which help us to envisage the processes involved, and to explain the differences between the various cases.

An incoming particle, when it collides with an atom, may do one of three things : it may undergo a collision with one or more of the orbital electrons ; it may collide elastically with the nucleus itself ; or it may produce some change in the nucleus, either raising it to an excited state or transmuting it. Only elastic collisions will concern us here. Inelastic collisions will in general produce a chemically different substance, and while this may be of great importance and should never be forgotten in the interpretation of results, this survey will not deal with effects primarily attributable to them.

In an elastic collision with an electron, the electron will usually be given enough energy to escape from its parent atom. However such displacements will produce no observable changes in a metal as the electron can return to its low energy state by passing its extra energy to the other electrons and the lattice as thermal movement. In insulating materials the displaced electrons may find themselves in the conduction band, as in the phenomenon of photoconductivity, or may be trapped and cause separation of the ions in an ionic substance, as in the photographic process. These effects can easily be produced by light, and the effects of radiation of other forms are generally similar. The phenomena are well known, and will not be further discussed.

In an elastic collision with a nucleus, a fraction of the energy of the incident particle will be transferred to the nucleus, and if this is sufficient it will cause the nucleus to escape from its lattice site. If the bombarding particle retains enough energy itself to escape from the lattice site, the site will be left vacant, although if the nucleus originally occupying it has not moved very far it may return spontaneously, or with the help of thermal fluctuations. If both the nucleus and the bombarding particle have moved away fast enough, the net result will have been to produce a vacant lattice site (henceforward referred to as a vacancy) and an interstitial atom. At a high enough temperature either the interstitialcies or the vacancies or both may diffuse through the lattice, and when a vacancy and an interstitial atom approach, they can recombine. It is also possible that vacancies or interstitials may aggregate into clusters, and if these are large enough they may collapse to form edge dislocation rings. (Screw dislocations cannot be formed in this way.) On this view, therefore, the effect of irradiation is to produce vacancies and interstitials in excess of the number which are in thermal equilibrium.

If the incoming particle has a very high energy, either the recoil atom or the incident particle itself may undergo further collisions with sufficient energy to knock atoms on. If the cross section for such collisions is large, a very large number of atoms may be displaced within a small volume. In this case it may be inappropriate to consider the damage from the point of view of individual vacancies and interstitials, and it may be more profitable to consider the effect as being equivalent to the release of a large amount of energy into the small volume, thus, momentarily, raising its temperature to a very high value. Such a local large injection of energy is frequently called a thermal spike.

Turning now to the macroscopic effects which nuclear displacements are expected to produce, we see that two major types of effect can occur. First, if the solid was previously in equilibrium that equilibrium may be disturbed. Thus a non-equilibrium number of vacancies and interstitials will appear, ordered alloys will become disordered and so on. If the temperature is low enough, these effects may not be able to anneal, and permanent damage will be produced, while if the temperature is high enough, the damage will rapidly anneal. Secondly, if the material was not previously in equilibrium, but was maintained in disequilibrium by its low temperature (as, for example, in the case of a quenched disordered alloy which would be ordered if slowly cooled), then the irradiation may actually make the material approach equilibrium. Thus when a vacancy interstitial pair has been formed and annihilated, the result may have been to produce a structure closer to equilibrium than it was before, for if such an approach to equilibrium is possible the train of events leading to it will be energetically more favourable than any other train.

## § 3. THEORY OF RADIATION DAMAGE

The theory of radiation damage in solids is not as yet in a very satisfactory form. Calculations of the nature and amount of the disruption produced fall into two parts, the calculation of the initial damage, and the estimation of the extent to which such damage is unstable and therefore anneals itself. In calculating the first stage of the process, the assumption is normally made that the collision between an incoming particle and an atom on a lattice site can be treated in the same way as a collision between two free particles, and that the main effect of the lattice is to prevent its atoms from being displaced unless they obtain energy larger than a certain critical energy $E_d$. The various attempts that have been made to produce a theory of the production of atomic displacements have recently been reviewed in detail by Kinchin and Pease (1955 b); here we shall just notice the kind of results obtained, without going into the details of the mathematical calculation.

The first estimates of the nature and amount of radiation damage were made by E. P. Wigner, and for this reason radiation damage is sometimes spoken of as the Wigner Effect. During the war, however, work on this subject was classified, and no unclassified references are available. The first major theoretical treatments of radiation damage to be made available were those of Seitz (1949) and Ozeroff (1949). Seitz's calculation has been criticized because it uses the Born approximation for collisions for which it is invalid, but it is frequently used to give order of magnitudes for the primary damage produced. Ozeroff's calculation, which is of the damage produced by neutrons and fission fragments, and the later calculations by Brinkman (1952, 1954) and Snyder and Neufeld (1954, 1955) are free from this objection. In the case of charged particles the theory shows that, if they are travelling above a certain speed depending on the bombarded substance, they lose most of their energy by electronic excitation, only about a thousandth being given to the nuclei. Below this critical speed, however, the greater part of the energy loss is given to nuclei in elastic collisions. If it is further assumed that a nucleus receiving energy greater than $E_d$ is always ejected, the actual number of vacancies and interstitials produced can be calculated. Roughly speaking, one vacancy interstitial pair is produced for each 50 to 100 ev of the energy which is lost in elastic collisions with nuclei. The critical speed for electron excitation is roughly the velocity of an electron having the ionization energy in the case of insulators, while for metals it is of the order of the electron velocity at the Fermi surface. The energy going into displacements can therefore be calculated for any individual case, and an estimate obtained of the number of vacancy interstitial pairs. In this calculation account can be taken of the possibility of knocked-on atoms colliding with further atoms to knock them on as well.

In the case of neutron bombardment, practically all of the neutron's energy is spent in knocking atoms on, which may move sufficiently fast themselves to cause electron excitation. The calculations show that neutrons cause 10 to 100 times more displacements in the higher energy ranges, because the electron excitation is much less. Thus a 2 MEV neutron will, on Seitz's theory, produce about 6000 displacements in aluminium, whereas a 5 MEV alpha particle will produce only 60, and a 20 MEV proton 80. Snyder and Neufeld (1955) have considered the theory of neutron irradiation in detail, and give as a rough rule that particles recoiling from collisions with neutrons lose about half their recoil energy in producing vacancy interstitial pairs if their energy is less than $e^2/\hbar$ while if their energy is above this, the energy given to producing vacancies and interstitials is approximately constant. They summarize their results in two formulae which give the number of vacancies or interstitials produced by a neutron of energy $E$ in a monatomic solid of medium or heavy atoms of mass $M$.

$$G(E) \sim (nE-\alpha)^2/4\alpha nE \qquad E \leqslant \gamma/n$$

$$G(E) \sim [(nE-\alpha)^2-(1-\overline{R})(nE-\alpha-\gamma)^2]/4\alpha nE \qquad E \geqslant \gamma/n$$

where $\gamma = Me^4/2h^2$, $n = 4M/(M+1)^2$, $\alpha$ is the binding energy of the atom in the lattice, and $\overline{R}$ is a slowly varying function of atomic number. An extension of this theory for polyatomic solids has been briefly reported by Harris (1955). In these calculations the possibility of the moving particle (which is usually itself a knocked-on atom) remaining in the vacant site has been neglected. This possibility has been taken into account by Kinchin and Pease (1955 a), who, however, neglect the loss of kinetic energy in the collision. They also obtain the result that half the kinetic energy of a moving atom not energetic enough to cause ionization will be given to producing vacancy interstitial pairs, though if the kinetic energy losses were taken into account it is probable that the fraction would drop to between a half and a quarter.

In all the above theories it has been assumed that the atoms having sufficient energy to escape will escape. If this is not true, fewer vacancy interstitial pairs will result, and Sampson, Hurwitz and Clancy (1955) have called on this to account for discrepancies with experiment that are referred to below.

For fission fragments, the energies are sufficiently large for the fragments to lose about the same amount of energy in that part of the slowing down process in which electron excitation predominates and in the remaining part, and the knocked-on atoms are energetic enough to produce about three additional displacements each. In this way it can be shown that a pair of uranium fission fragments produce about 25 000 displaced atoms.

A further important point in radiation damage is that it is usually far from homogeneously distributed, either macroscopically, because of lack of penetrating power of the charged particles, or microscopically, because large numbers of vacancies and interstitials are produced by one particle whether neutral or charged. These effects can be avoided by bombarding with high energy electrons, which can only cause one vacancy and interstitial per electron, and also have greater penetrating power. However, the number of defects produced by electrons is much smaller than that produced by available sources of other particles. Electrons also lose a large amount of their energy in other ways, so that the ratio of heat produced to displacements is much larger than for other particles. For both these reasons electron bombardment is primarily a specialized tool: examples of its use will emerge later. Gamma rays have very little direct interaction with nuclei, and thus the main displacements during gamma irradiation are produced by the electrons recoiling from Compton collisions. This effect is not so small as might at first be expected, and measurable effects have been reported by Dugdale (1955). The damage should be reasonably uniformly distributed, and can affect a greater thickness of material than can be damaged using electrons as the primary bombarding particles.

For heavy charged particles it is possible to overcome some of the disadvantages of the short range by using very thin specimens, although even here the majority of the damage will occur near the end of the particle range, while if the specimen is thinner than the range, the majority of potential damage will be lost and the ratio of electron excitation (and hence heat) to damage produced will rise by a factor of several hundred. Schwed and Groetzinger (1952) have suggested a device which introduces an absorber into the beam so that the thickness of absorbing material traversed by the particles before reaching the specimen varies linearly and periodically between zero and the range of the particles.

Another approach to the problem of irradiation damage has been given by Brinkman (1952, 1954). He envisages that, while a fast moving atom will produce vacancies and interstitials as the primary form of damage, once the atom has become slow enough, the amount of energy spent in non-displacing collisions will be so large that a whole region may be considered to melt and refreeze. This he claims to be different from earlier thermal spike concepts in that the high initial density of vacancies and interstitials will anneal more or less completely, and the damage will be left as dislocation loops and small volumes of new orientations. Brinkman refers to such a volume as a displacement spike, and calculates that with heavy atoms this will be the only important form of damage, while in the light elements the vacancy–interstitial form will predominate, owing to the much lower energy needed before overall melting occurs. The validity of Brinkman's deduction that vacancies and interstitials are almost eliminated depends on the metal cooling from its high temperature sufficiently slowly for them not to be frozen in. It does not seem that this would in general be the case. If it is, then the easy annealing of a certain amount of damage would be due to the collapse of dislocation rings of varying diameter. If it is not, then the 'displacement spike' is a small region of the crystal that has been effectively melted and quenched.

Another special case has been considered by Smoluchowski (1954, 1955), who has pointed out that at very high energies (∼400 MeV) the number of nuclear 'star' collisions may be sufficient to cause the number of displacements to rise with increasing energy.

## § 4. ANNEALING OF RADIATION DAMAGE

If, after irradiation at a low temperature the specimen is heated, then any radiation damage which is in the form of unstable configurations, such as large numbers of vacancies and interstitials, will tend to anneal out. Studying the kinetics of the recovery, therefore, provides a method for investigating the nature of the damage and also gives information on the behaviour of the various types of lattice disorder. Most of the theoretical work on the annealing of radiation damage has been done to explain particular experimental results, and examples of these theories will be found at the appropriate place in the experimental sections which follow. At this stage it will be sufficient to refer to one or two of the more recent of these attempts, in order to see what type of processes are envisaged. Fletcher and Brown (1953) have pointed out that if the damage to be annealed consists of vacancies and interstitials, three types of recovery process are possible. For the first, the interstitial and vacancy are separated by a short distance and recombine when the temperature is raised sufficiently ; this gives a monomolecular type of rate process or a sum of several such processes. For the second, the interstitial and vacancy are sufficiently far apart for there to be a finite chance of their escaping from each other's influence ; in this case the appropriate capture function is more complex. For the third, those vacancies which escape from their interstitials (Fletcher and Brown only consider this case) diffuse and either recombine with other interstitials, which gives a bimolecular rate equation, or else drift to surfaces or dislocations. Hence the annealing of isolated vacancy–interstitial pairs is the sum of at least three terms. Comparison of the results of this theory with experiment will be deferred to § 12.

Another theory of the annealing of lattice defects has been given by Dienes (1953 c) to account for the observations made on the recovery of the resistivity of copper. He suggests that the activation energy for recovery varies with the number of lattice defects present. Such a variation would not change the nature of a plot of log $t$ versus $1/T$, where $t$ is the time to a given state of anneal and $T$ is temperature, but it would systematically change the slopes of such plots for different amounts of anneal. This is similar to the effect observed if the activation energy is constant but the order of the rate process higher. A similar apparent increase in the order of the process occurs if the defects are not originally uniformly distributed, as has been pointed out by Marx (1953). An explanation of annealing in terms of dislocation loops was mentioned in § 3.

It is, of course, only at temperatures at which annealing does not occur at an appreciable rate that large effects due to the build up of damage considerably in excess of equilibrium are to be expected, as emphasized by Rothstein (1953 a, b), who has calculated the amount of damage which will be present in the steady state reached during irradiation. The result of the low rate of annealing at low temperatures will be to give ‘ anomalous ’ values to many physical properties, so that materials which have reached a steady state in a pile will show many of the effects normally associated with high temperatures when the ambient temperature is lowered.

A further form of annealing must also be considered in irradiation. this is annealing caused by the irradiation itself. Quite apart from local temperature increases, the bombarding particles and the knocked-on atoms may in some way annihilate defects already present, as well as producing more. Various mechanisms for this have been discussed by Barnes and Makin (1955).

## PART II. EXPERIMENTAL MEASUREMENTS OF IRRADIATION EFFECTS

The experimental techniques used to irradiate solids are many and varied, and it is not intended to survey them here. However, some papers devoted to techniques may be referred to. The Atomic Energy Research Department of North American Aviation have prepared a series of papers on cyclotron techniques for studying radiation effects, particularly at low temperatures (Yockey, Fillmore, Hunt, Andrew, Glasgow, Weber, Jeppson, Pepper and Carter 1952, in shorter form Yockey, Andrew, Fillmore, Glasgow, Hunt and Pepper 1954), and descriptions of reactors specially designed for testing materials are given by Huffman (1954) and O'Connor and Foster (1954). Special x-ray cameras for studying irradiated material, which may itself be highly radioactive, have been described by Cummings, Kaulitz and Sanderson (1955), and by Bredig, Klein and Borie (1955). The experimental conditions for the various experiments are summarized in table 5 (p. 454).

### § 5. RADIATION EFFECTS ON THE ELECTRICAL RESISTANCE OF PURE METALS

One of the best indicators of the degree of perfection of a crystalline lattice is its electrical resistivity. Results obtained from experiments on the resistivity of cold-worked metals have shown that this property recovers at a lower temperature than some of the mechanical properties such as hardness. This has led to the belief that hardness is primarily concerned with the number and configuration of dislocations in the material, while resistivity is more a measure of the number of vacancies and interstitials. If this view is correct, resistivity should be markedly affected by irradiation, and the temperature and characteristics of this annealing should in turn verify or deny the correctness of the view that the resistivity change of a cold-worked metal is primarily due to vacancies and interstitials.

The first systematic study to be reported was made by Martin, Austerman, Eggleston, McGee and Tarpinian (1951), who irradiated aluminium and copper (as well as copper–gold alloys, which will be dealt with later) with alpha particles from the Berkeley cyclotron. When the samples were irradiated at −150°C, large changes were found in the electrical resistivity of both metals, and these changes began to anneal out as low as −80°c. If the specimen was brought back to room temperature, no change was found in the resistivity, or its temperature coefficient, from their values before irradiation, although, as we shall see later, the hardness of copper was still appreciably changed. Since cold work normally produces resistivity changes in copper at room temperature this result implies either that the additional resistivity is due to dislocations or that the vacancies and interstitials produced in radiation damage are closer together than those produced in cold work, or that in cold work more vacancies are produced than interstitials (or vice versa) and hence complete annealing by recombination is impossible. This latter explanation is highly probable, as the energy needed to form an interstitial atom is high compared with that needed to form a vacancy, whereas, once formed, an interstitial is much more mobile—in radiation damage it is most probable that it is the interstitial mobility which is responsible for most of the annealing of resistivity. A calculation by Huntington (1953) has yielded $\frac{1}{4}$ ev as the activation energy.

If the additional resistivity is in fact due to scattering by interstitials and vacancies, it should be independent of temperature provided no annealing occurs, and hence a much larger percentage change in the residual resistivity at low temperatures is expected after irradiation. This was observed by Randolph (1952, 1953) who found that while the room temperature resistivity change of molybdenum was only 4%, it was 200% at 1·2°K. In both cases the measurements were made after bombardment at −100°c, so that some annealing had probably occurred in the room temperature specimens. Subsequently, in a more careful experiment, Overhauser (1953 b) has found that, apart from annealing effects, the additional resistivity caused by deuteron bombardment is independent of temperature in the range from −125°c to room temperature.

Bowen and Rodeback (1953 a, b) have reported conflicting results. In their experiments the change of electrical resistivity was measured as a function of temperature after bombardment and also after cold work. Using a formula of Gruneisen this enabled them to obtain values for the change in Debye temperature. For the irradiated copper they found that, although there was a large change in residual resistance, there was also a change in the temperature dependent part amounting to a change of 45° in Debye temperature. On annealing, both the temperature dependent and independent parts recovered, and a smooth curve was obtained by plotting the components one against the other. For cold-worked copper the curve of residual resistivity versus change in Debye temperature was very similar to the irradiated case.

The implications of this analysis are that, as a result of the internal stress caused by the radiation damage, the spectrum of lattice oscillations is shifted to lower frequencies, and hence more energy will be stored in the thermal oscillations of the lattice. This energy could well account for a large part of the energy stored in irradiated or cold-worked materials. The interpretation of the temperature independent part in terms of point and boundary scatterers has been discussed by Rodeback (1954).

The variation of radiation-induced resistivity from metal to metal has not been investigated very systematically. Wruck and Wert (1954 a, b, 1955, Wruck 1954) carried out experiments on iron, nickel and cobalt to see if the crystal structure had any large effect, as these metals have similar properties from most other points of view. After bombardment at $-150°$c with $10^{17}$ deuterons of 10 mev per cm$^2$ the increase in iron was 50% while that in cobalt and nickel was 10%. Similar results were obtained with neutron bombardment at room temperature. This implies that the effect is greater in the body-centred cubic lattice than in either of the close packed lattices.

Kinchin (reported in Dugdale 1955) has studied the changes in resistance of tungsten, molybdenum and platinum irradiated in a hollow uranium slug (to increase the number of fast neutrons) to doses of about $10^{19}$ fission neutrons per cm$^2$. The resistance change in tungsten was about 10% and that in molybdenum about 7%, whereas platinum showed a much smaller change ($\sim$1% at $5\times10^{18}$ nvt* and $\sim$2% at $1{\cdot}5\times10^{19}$ nvt). Wruck and Wert (1955) have also studied titanium (hexagonal) and vanadium (body-centred cubic). These showed a very large change in resistivity compared with the changes in iron, nickel and cobalt, but, as their initial resistivity is so much higher the effect of expressing the result as a percentage is to bring the change in titanium down to that in cobalt, and to make vanadium least changed of all. As the largest percentage change, that in iron, anneals much more rapidly than the change in the other metals, the total result of this study is rather inconclusive.

The magnitude of the effect after long bombardment at a low temperature has been studied by McReynolds, Augustyniak, McKeown and Rosenblatt (1954, 1955). After $1{\cdot}1\times10^{19}$ nvt at $-195°$c the change of resistivity of copper is 20% and that of aluminium 33%.

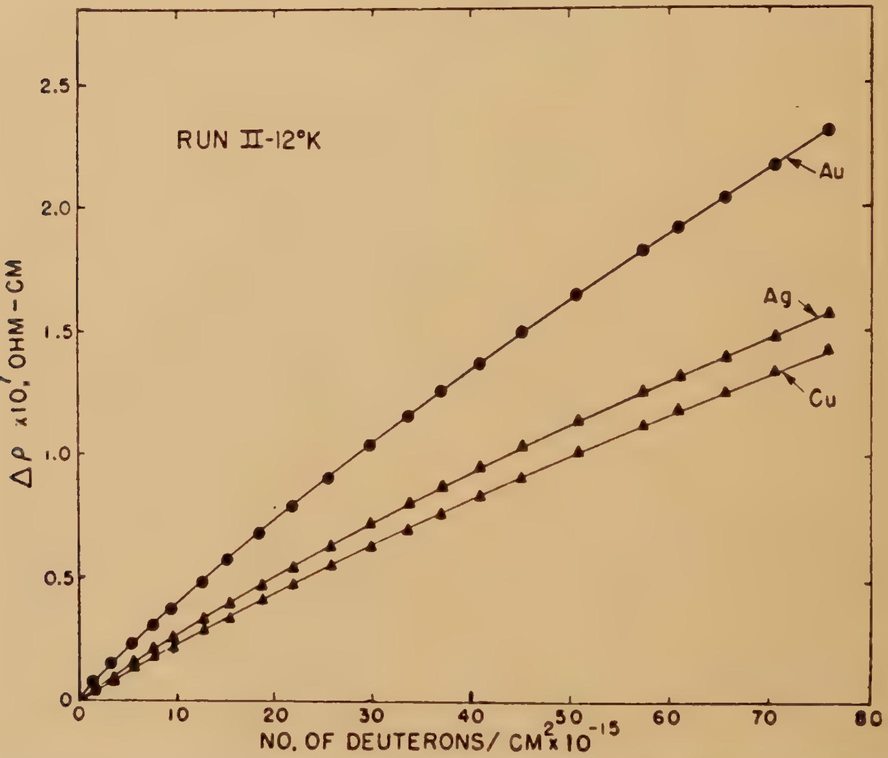
The lowest temperature that has so far been used for radiation studies is 10°k ($-263°$c). Cooper, Koehler and Marx (1954, 1955) have bombarded copper, silver and gold wires at this temperature. They found that the resistivity increased at a rate that decreased as the bombardment proceeded, as shown in fig. 1, and also that the resistivity–flux curves were different at 12°k and 16°k. The first effect could be due to bombardment annealing, and has been discussed in this connection by Barnes and Makin (1955), but the second, if real, would seem to indicate a thermal annealing at these temperatures. However, Cooper, Koehler and Marx found no change in resistivity if the specimens were left for a time at the bombardment temperature.

---

* The unit nvt is frequently employed in reactor irradiation to measure the integrated flux in neutrons per cm$^2$.

Using very high energy protons as the bombarding particles (100 to 400 Mev), Pearlstein, Ingham and Smoluchowski (1955) have bombarded thin tungsten wires in a proton synchrotron up to doses of $10^{16}$ protons per cm$^2$. At this stage the resistivity of the wires had changed by 0·3% (260 Mev) to 0·71% (410 Mev). At these high energies, it is suggested (Smoluchowski, Pearlstein and Ingham 1955) that the particles emerging from nuclear disintegration 'stars' are an important source of damage, and a calculation based on this assumption gives reasonable agreement with the observed results, whereas on the Seitz theory, the damage should be proportional to the reciprocal of the particle energy for such thin specimens.

Fig. 1



Resistivity increase of copper, silver and gold during bombardment with 12 Mev deuterons at 12°K. (Cooper, Koehler and Marx 1955.)

Other determinations of the magnitude of the resistance change in metals caused by irradiation have been made in experiments designed also to study the annealing of this change. These are discussed below in § 7.

One further experiment will be discussed in this section. It is one of five which have been performed to determine the energy required to produce radiation damage in a metal, and is in fact the third in time.

In all of these experiments, electrons have been used as the bombarding particles as in this case the amount of energy transferred to an atom is comparatively small. If the electron energy is varied from about 0·1 to 1·0 MEV (as can be done conveniently in a Van de Graaff generator), then the maximum energy given to an atom (corresponding to a head-on collision) will vary from about 5 to 50 ev. This is of the order of magnitude of the energy necessary to dislodge an atom from its position in a lattice. The experimental method is therefore to bombard at varying energy and look for a threshold value below which no effect is observed. Eggen and Laubenstein (1953) have done such an experiment in copper, using the resistivity as the observed property. The specimens were thin copper strips, and they were irradiated at liquid air temperature. The zero damage intercept on a plot of rate of change of resistance against electron energy occurred at $0{\cdot}49 \pm 0{\cdot}02$ MEV which corresponds to a displacement energy of $25 \pm 1$ ev in copper. A detailed analysis of the errors of this figure is not possible until more details of the experiment are available.

## § 6. Radiation Effects on the Electrical Resistance of Alloys

Similar effects to those occurring in pure metals are expected also in alloys, but here other phenomena may also occur. Unstable phases such as occur in precipitation hardening alloys may be expected to decompose under the action of the radiation, while special effects may also be expected in superlattice structures.

Billington and Siegel (1950) and Murray and Taylor (1952, 1953, 1954) have studied the effect of neutron bombardment on a supersaturated solid solution of beryllium in copper as well as other precipitation hardening and unsaturated solid solutions. The results on copper–beryllium showed that the increase of resistance due to neutron bombardment is larger in this alloy than in pure copper or in most other alloys (including some hardening ones). This is interpreted by Murray and Taylor as being due to the formation of nuclei of the stable phase, an explanation which is also in agreement with most of the measurements on other properties. The effect of room temperature irradiation is thus similar to the effect of a low temperature anneal—say at 75°C—which also increases the resistance by producing small nuclei of the precipitating phase, but the two effects are not completely identical. Low temperature ageing increases the resistance much more rapidly in polycrystals, a fact usually attributed to preferred nucleation at grain boundaries; but Murray and Taylor's experiments showed that the change of resistivity on irradiation is the same in both single and polycrystalline samples. This they attribute to nucleation at random, not in this case at grain boundaries, probably caused by the greater ease of microdiffusion due to the excess number of vacancies and interstitials introduced during irradiation. Richards (1955) has pointed out that the effects of irradiation are perhaps more like those of cold work than those of low temperature ageing. Murray and Taylor attribute their failure to find similar effects in other precipitation hardening alloys to one or more of the following causes :

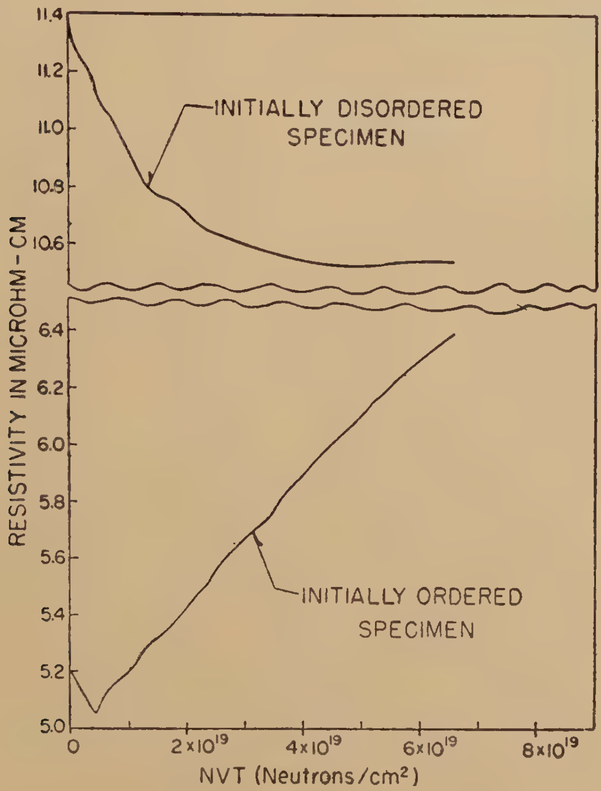
(1) The base metal may not be heavy enough for large numbers of displacements per incident neutron.
(2) The activation energy for diffusion may be too low.
(3) The size of nucleus needed for stability may be too large.
(4) The nuclei may be too small to affect the resistivity.

This interpretation of the large resistivity change in copper–beryllium has been confirmed in an experiment of Cleland, Billington and Crawford (1953). They irradiated solution quenched copper–beryllium alloys in a graphite reactor at ~120°K and at ~300°K. They found that the increase in resistivity at ~120°K was only a quarter that found if the same irradiation were given at 300°K. However a short subsequent irradiation at 300°K increased the resistance to the value that would have been expected had the entire irradiation occurred at 300°K. This is taken to imply that the greater portion of the resistance increase is due to a process depending on thermal activation, such as microdiffusion.

The alloys which can develop a superlattice structure, behave similarly to the precipitation hardening alloys. Two conditions can exist at low temperatures ; one in which the metal has been slowly cooled and is in an ordered state, the other in which the metal, having been quenched from above the transition temperature, is disordered. Radiation damage will therefore have two effects, the interstitials and vacancies formed may fall back into different sites thus tending to disorder a completely ordered alloy, but, on the other hand, there will be a tendency for them to fall back into sites with short range order, thus possibly ordering a disordered specimen. The first experiment of this kind to be reported was made by Siegel (1949). He found that fluxes of up to $3{\cdot}3\times10^{19}$ neutrons per cm$^2$ increased the resistivity of the ordered alloy from 4·6 to $10{\cdot}1\times10^{-6}$ ohm cm while hardly changing that of the disordered one—it increased from 11·2 to $11{\cdot}3\times10^{-6}$ ohm cm. This he interpreted in terms of disordering by bombardment. The small change in the resistance of the disordered sample being completely accounted for by the transmutations produced. A similar result was obtained by Martin *et al.* (1951) bombarding both $Cu_3Au$ and CuAu at −150°C with $\alpha$ particles ; again the ordered samples showed large increases while the disordered samples were relatively unaffected. Measurements of the lattice parameters confirmed the interpretation, being particularly convincing in CuAu, where the tetragonal ordered cell became completely cubic after 33 microamp hours. On the other hand Adam and Dugdale (1951) found that irradiating ordered copper–gold alloy with ‘ slow ’ neutrons at first gave an increase of order, as shown by the unit cell dimensions, satellite reflexions to the superlattice lines, and a decrease in electrical resistivity. At a later stage the resistivity again increased, but the superlattice lines showed no signs of disappearing.

The change of resistivity during bombardment has been studied more closely by Glick, Brooks, Witzig and Johnson (1952). Bombarding $Cu_3Au$ with neutrons at 80°c, they found, as shown in fig. 2, that an initially ordered sample of resistivity 5·2 micro ohm cm at first showed a rapid drop of resistivity, with a minimum 3% below the initial value at an integrated flux of $0{\cdot}4 \times 10^{19}$, and then rose approximately linearly, reaching a value 60% above the original at a total flux of $20 \times 10^{19}$. An initially disordered sample decreased continuously in resistivity to a value 7·5% below the original at $5 \times 10^{19}$ nvt, then and slowly increased to a value 4·2% below its initial value after about $20 \times 10^{19}$ nvt. These results have to be interpreted by assuming that both disordering and ordering can be caused by irradiation, the later rises in resistivity of the initially disordered sample being attributed to mercury impurity formed from gold during bombardment, more than 1% of which will have been transmuted by the end of this experiment. The initial drop in resistivity of the ordered sample is more puzzling; it is presumably due to an

**Fig. 2**



Resistivity of initially ordered and initially disordered $Cu_3Au$ during neutron irradiation at 80°c. (Glick, Brooks, Witzig, and Johnson 1952.)

increase in order due to greater diffusion when irradiation starts, but stopping when sufficient atoms have been knocked on to disrupt the superlattice seriously. In line with these explanations are the results of another experiment of Glick and Witzig (1953). Specimens were irradiated at 140°c where the diffusion rate would have been more rapid. An initially ordered sample showed a resistivity drop of 6% at $0{\cdot}4\times10^{19}$ nvt followed by a slow increase to a value 4% above its initial at $14\times10^{19}$ nvt, while an initially disordered sample showed a resistivity decrease which saturated at about $2{\cdot}5\times10^{19}$ nvt at a value 17% below its initial: a control experiment at this temperature showed that a disordered sample loses only 4% of its resistivity without irradiation.

Simultaneous measurements of hardness and x-ray patterns were made by Fillnow, Halteman and Mechlin (1953). Both ordered and disordered samples increased in hardness. Though no change in the x-ray pattern of disordered material occurred, the ordered sample gave a pattern whose lines were sharpened by irradiation and whose long range order parameter decreased only slightly. No changes of lattice parameter occurred in the disordered material; a significant decrease occurred in ordered material.

The bombardment of $Cu_3Au$ has also been studied by Blewitt and Coltman (1952). Bombarding at 200°c with a flux of $10^{12}$ neutrons/cm² sec, they found that the resistivity decreased steadily. When the pile was switched off the resistivity fall dropped after a time lag of 12 hours compared with a relaxation time of $10^5$ hours for unbombarded material at this temperature. This effect makes it almost certain that defects are mobile in the bombarded substance, and allows an estimate to be made of the mean path travelled by an interstitial and vacancy before recombination of a vacancy–interstitial pair. The experiments on the disordering of ordered $Cu_3Au$ imply that $10^4$ atoms are affected for each collision. From the tendency towards saturation of the ordering process in about one month at a total flux of $10^{18}$ neutrons/cm², it follows that if a figure is assumed for the fast neutron cross section, say 3 barns, then the total number of atoms displaced by incident neutrons can be calculated. This comes out to be $10^{17}$. As the total number of atoms per c.c. is about $10^{23}$ this implies that each neutron collision 'affects a volume containing $10^6$ atoms, producing in it the saturation state. As this is larger than the $10^4$ atoms actually displaced, Blewitt and Coltman infer that the average vacancy and interstitial migrate appreciably before recombination, causing some ordering on the way. The discrepancy between the saturation flux found by these workers and that found by Glick and co-workers at a lower temperature is presumably due to the reduced mobility of the vacancy–interstitial pairs at the lower temperature, though the total ordering, and hence resistivity change, produced per vacancy–interstitial pair should not be a function of temperature provided the vacancy–interstitial pairs all annihilate in a similar way. Another prediction that can be made from the hypothesis that the ordering is produced by the migration of interstitial–vacancy pairs, is that the ordered regions should be of the order of size of the domain ordered by one initial particle, i.e. about 100 Å. If at saturation the material is assumed to consist entirely of ordered domains, then the mean size can be estimated from the resistivity to be about 65 Å, while, in a second paper, Coltman and Blewitt (1952) report that x-ray measurements of the superlattice line breadth correspond to a mean size of 125 Å. Finally Coltman and Blewitt (1953) report that multiplying the flux by a factor 4 accelerated the approach to order by a factor 4, while another sample, bombarded at −150°C, which was initially of the degree of order in equilibrium at 376°C, gave no decrease of resistance (as occurred if the bombardment were made at 150°C), but rather a slight decrease. Subsequent annealing of this specimen gave the expected decrease of resistance.

A similar experiment has been reported by Dixon and Bowen (1954) for $Cu_3Au$ irradiated with 36 MeV alpha particles. If an ordered alloy was irradiated at −180°C the initial disordering rate was $3{\cdot}3 \times 10^{-17}$ micro-ohm cm per $\alpha$ particle/cm$^2$, while bombardment at 220°C gave a disordering rate smaller by a factor 6. This implies that vacancies and interstitials are mobile at the higher temperature and re-order most of the disordered material. The ordering rate at 220°C would account for only 5% of the difference.

All of these experiments are consistent with the theory that the ordering of disordered alloys occurs only by the diffusion of vacancies or interstitials and that, if the temperature is low enough, the effect can be prevented. This means that the ordering of disordered alloys is a process more akin to the annealing of radiation damage in pure metals than to its production.

While we have now given at least a quantitative explanation of the ordering effect of irradiation, we have not discussed the disordering. The magnitude of the effect is too large for it to be accounted for entirely by ‘quenching’ from the thermal spikes. Two possible theories have been proposed. One, by Kinchin and Pease (1955 a) attributes the disordering to the large number of collisions in which moving atoms change places with stationary ones, thus in each collision replacing an atom of the ordered lattice by an atom chosen at random. The other theory, due to Seitz (1955), attributes the disordering to the plastic strain arising from the thermal stresses around displacement spikes.

In neutron irradiation in a pile one cannot control closely the exciting energies. A more certain way of investigating these effects is to produce the damage by irradiation with high energy electrons. This not only eliminates effects due to transmutations, but also avoids the concentration of large amounts of damage into small volumes, for the number of secondary collisions will be much smaller. This experiment has been done by two teams. At Harwell, Adam, Green and Dugdale (1953) found that irradiating with 1 MEV electrons produced no change on the resistance of an ordered specimen, but that subsequent annealing at 100°C or 130°C reduced the resistance by about 2%. They interpret this as follows. The fully annealed 'ordered' sample corresponds to a degree of order in equilibrium at about 250°C. The addition of vacancies and interstitials allows some rearrangement to occur at a lower temperature, and hence a greater degree of order to be obtained. An analogous experiment using gamma rays as the bombarding radiation has been reported by Dugdale (1955). The displacements probably come from collisions with electrons which have interacted with the gamma ray. The advantage of this method of producing displacements is that they will be more homogeneously distributed than with direct electron bombardment. The annealing of such specimens is being studied.

A similar experiment has been carried out at North American Aviation by Dixon, Meechan and Brinkman (1953). As well as repeating the observations of Adam, Green and Dugdale, they irradiated at −195°C with a total of $3{\cdot}4\times10^{19}$ electrons to see if any disordering would be produced. No change of resistance was found, however, and on annealing at room temperature for 50 hours a drop in resistance (measured at −195°C) of 2·7% was found, followed by fluctuations in excess of experimental error (∼1%). The lack of any increase of resistivity not only implies that no disordering has occurred, but also that some of the vacancies and interstitials produced must have recombined even at this low temperature. Thus there appears to be a fundamental difference between electron and neutron or alpha particle damage in that the former cannot produce disorder in an ordered alloy. This is very reasonable, as none of the mechanisms for disordering mentioned above could possibly occur during electron bombardment, except, perhaps, a small number of replacement collisions. In fact with electron bombardment each vacancy and interstitial is virtually isolated, and there is less tendency to produce disorder than there is when the metal is annealed and slowly cooled.

A non-equilibrium number of imperfections can also be produced in other ways. A quench from a high temperature will give a number of vacancies corresponding to the high temperature, but will, of course, leave the alloy disordered, nevertheless a comparison between the activations for ordering should be possible. A quench from just below the transition temperature should give an ordered alloy, rather far from perfect order and with a non-equilibrium number of vacancies. Finally cold work is also believed to introduce vacancies and interstitials primarily by the movement of dislocations through one another. It is thus possible to create various states which in some way resemble radiation damage. Dugdale and Green (1954) have therefore investigated the effect of a quench from 380°C, i.e. just below the critical temperature, and of deforming at room temperature, on the annealing behaviour at 100°C. In both cases an increase in ordering was observed, and as in the case of irradiation, it could be accounted for by vacancies moving with an activation energy of 0·9 ev.

Stello (1952) also investigated the relative ordering rates in CuAu after various treatments. The cold worked specimens could not be regarded as ordering with a single activation energy while the thermally disordered specimen could. After bombarding with 40 Mev α-particles the ordering, if it could be regarded as a single process, had an activation energy 20% higher than that of thermally disordered specimens.

The best study of the various ordering processes has been made by Brinkman, Dixon and Meechan (1953, 1954). They point out that a gold interstitial has an energy probably 5 ev higher than that of a copper interstitial, and thus the chance of a copper interstitial moving into a site occupied by a gold atom and displacing the gold atom to an interstitial position is quite negligible. This means that the migration of interstitial atoms cannot accomplish ordering, and so the observed ordering in $Cu_3Au$ is almost certainly due to vacancy migration. This conclusion is confirmed by observations on the ordering rate of $Cu_3Au$ quenched from various temperatures ; in which ordering occurs in the same temperature range, and at a rate that increases with the temperature from which the material has been quenched, i.e. with the number of vacancies present. On this hypothesis, Brinkman, Dixon and Meechan interpret the results of bombardment of $Cu_3Au$ as follows.

In electron bombardment at low temperatures an equal number of vacancies and interstitials are probably produced. At a low temperature the interstitials become mobile and annul some of the vacancies, but some interstitials will move to boundaries leaving a few vacancies available for ordering if the temperature is raised. If the sample was initially ordered these vacancies will be efficient at producing additional order in the large domains already present. In electron bombardment at higher temperatures both vacancies and interstitials will be mobile and the vacancies can again produce ordering, particularly if a large degree of order is already present. The situation differs from that produced by quenching in that multiple vacancies are not present and that interstitials occur.

Cyclotron and pile irradiation at low temperatures produce vacancies and interstitials in much greater numbers than electron bombardment, and also other lattice imperfections, such as the disordering caused by heavy localized displacement. The interstitials will, as before, become mobile somewhat below room temperature and will annihilate the vacancies, except for a small number which go to boundaries, dislocations and similar sinks. The number of vacancies left will thus be about the same as in electron bombardment, and these will be available for ordering if the temperature is raised to about 150°c. This effect will be much more efficient in an initially ordered specimen, as it is much easier to order using a single vacancy if a partially ordered domain is available. To order a disordered sample it is necessary actually to irradiate at a temperature at which both vacancies and interstitials are mobile, when many more vacancies are available for ordering.

This deduction is in full accord with the experimental facts. Brinkman, Dixon and Meechan bombarded $Cu_3Au$ foil at −100°C with 9 MEV protons. This increased the resistivity by 4·25 micro ohm cm after a flux of $5\times10^{17}$ protons per $cm^2$ as compared with 0·65 micro ohm cm for a disordered specimen, implying that 3·60 micro ohm cm is due to disordering. Both ordered and disordered specimens lost 60% of the increased resistivity in the temperature range up to 0°C, which is the range in which as we shall see, most of the extra resistivity of pure copper is lost. No ordering of the disordered specimen occurred in this temperature range either in this case or in electron bombardment experiments, for the resistivity of a disordered specimen after bombardment followed by pulse anneals up to 130°C was still above its initial value. The change in the resistivity of the ordered specimen was about the same up to 0°C, which seems strong evidence in favour of interstitial migration as the process occurring at this temperature. This evidence will be used in the next section to interpret the annealing effects in pure metals. Brinkman, Dixon and Meechan have confirmed with proton bombardment that no ordering of disordered samples occurs on annealing up to 200°C, but that bombardment at 200°C does give an enhanced ordering rate, as also found by other authors (Adam and Dugdale 1951, Glick *et al.* 1952, Blewitt and Coltman 1952).

A further experiment on the copper–gold alloys $Cu_3Au$ and CuAu has been done by Cook and Cushing (1953 a, b), who interpret their results somewhat differently. They irradiated their samples in the Canadian N.R.X. pile under three different conditions. The first set were irradiated in uranium with cadmium shielding to give a high fast neutron flux with no thermal neutron component, the second set were irradiated with the normal reactor spectrum and the third set were irradiated in the reactor spectrum with cadmium shielding to filter out the thermal neutron component. They found that the fast neutron flux disordered the ordered specimens, but did not greatly affect the disordered specimen, whereas the thermal neutron component reduced the resistivity, and hence presumably ordered, both ordered and disordered samples, at least at first. This deduction was made by the difference of the effects in the second and third sets.

They interpret the results of fast neutron bombardment in terms of thermal spikes giving disordering, and hence obtain excellent agreement between theoretical and experimental curves. Using a reasonable value (5 barns) for the average total scattering cross section for fast neutrons, they find that a single spike disorders $10^4$ atoms. They interpret the ordering effects by attributing them entirely to the mercury produced by transmutations caused by the thermal neutrons. This is reasonable in their case if their experiments show that only thermal neutrons produce ordering, as capture is the main process undergone by thermal neutrons, but it is totally impossible to explain on these grounds the experiments described above whereby electron and proton bombardment also gave an increase of the amount of order. Also, as Cook and Cushing admit, one would *a priori* expect an impurity atom to give an increase of resistivity. It seems probable that Cook and Cushing observed no ordering in the disordered alloys because their bombardment temperature was too low, and that the initial drop in the resistivity of ordered alloy in the thermal neutron flux was here, as in other experiments, due to ordering caused by vacancy migration. Why they observed no comparable dip in experiments with a cadmium filter is a little obscure. Dugdale has found a drop of resistivity in an ordered sample of $Cu_3Au$ bombarded in BEPO at 50°C through a cadmium shield. Blewitt and Coltman (1955) have criticized Cook and Cushing's interpretation in more detail. They point out that effects can be observed when the concentration of mercury atoms is only about $1:10^8$ atoms. Blewitt and Coltman attribute the difference found by Cook and Cushing between experiments with and without the converter by assuming that the increased fast neutron flux with the converter in place gives on the whole fewer total jumps for the vacancies to be annihilated despite their greater number, probably because of the clustering of defects.

The only other order–disorder alloys which have been studied for radiation effects are brass and nickel–manganese. Eggleston and Bowman (1953) have irradiated beta brass with alpha particles at −100°C. Beta brass cannot be disordered by quenching from above the transition temperature, presumably because of the high relaxation rate at temperatures well below the transition temperature, but the large increase of resistance caused by irradiation (about four times the percentage increase in copper under the same conditions) makes it very probable that the irradiation succeeded in producing some disordering. The fact that the additional resistance anneals out rapidly at about −40°C makes this interpretation very plausible.

The effect of fast neutron pile irradiation on alloys of nickel and manganese between 16·5 and 31·9 at. % manganese has been investigated by Aronin (1953, 1954). These alloys are ferromagnetic when ordered in the $Ni_3Mn$ superlattice, and Aronin has supplemented his resistance measurements with measurements of magnetic induction. As in $Cu_3Au$ he found that the resistance of ordered alloys increased on bombardment, and the interpretation in terms of disordering was confirmed by the decrease of intrinsic magnetic induction. At low atomic percentage manganese, about 16 to 22%, the reduction of inductance and increase of resistance is not as fast as expected, and this is attributed to the intrusion of another effect; for bombarding thermally quenched alloys of this constitution gives a large increase of magnetic induction and of the temperature coefficient of resistance as well as a sizeable decrease of resistance, whereas small changes in the opposite direction are observed in similar experiments on alloys with greater manganese content. These changes are quite different from the effects produced by cold work, which are frequently of opposite sign. It is tempting to think that the large changes in the disordered structures are caused by ordering due to vacancy movement, but why this only occurs for alloys of less than 22% is not clear; perhaps these alloys have more natural vacancies than the stoichiometric alloy.

For the stoichiometric alloy (25% Mn), Aronin has studied the effects of bombardment on thermally disordered samples, and also cold-worked disordered samples. These both tend toward another state of intermediate properties. The bombardment of ordered $Ni_3Mn$ can also be interpreted theoretically as an exponential variation of order parameter with flux, if (as is reasonable theoretically) the order parameter varies linearly with induction and quadratically with resistance. Aronin has analysed Siegel's results on $Cu_3Au$ assuming that the extra resistance is proportional to the square of the order parameter, and shows that these are also consistent with an exponential variation of order parameter. Another calculation possible on these grounds shows that one neutron of 1 MeV effects the replacement of 5000 atoms in the disordering process, that is to say a region about 70 Å in diameter.

It has been pointed out by Smoluchowski that the reduction of resistivity resulting from the bombardment of alloys might not be due to a change in the degree of order, as it could also follow a change in the Debye temperature due to a change in elastic constants. Such a change should affect the temperature dependent part of the resistivity. To check this Rosenblatt, Smoluchowski and Dienes (1954) have irradiated alpha brass of various compositions (10, 20 and 30% Zn) in a pile. Since alpha brass is presumably a random alloy, it might be thought that any decrease in resistivity would be due to changes in the elastic constants. A decrease is, however, observed not only at room temperature but also at liquid hydrogen and liquid helium temperatures, and so the Debye temperature explanation cannot be adequate. Annealing experiments showed that the resistivity returned to its unirradiated value at about 170°C. Keating (1954 a, b) found no signs of order in the x-ray or neutron reflections from a 70–30 brass crystal annealed at 190°C. His data implied that the critical temperature must be at least as low as 95°C, while the drop of resistivity during room temperature irradiation would seem to indicate that some degree of order is stable at that temperature.

## § 7. ANNEALING OF THE EXTRA RESISTANCE CAUSED BY IRRADIATION

In the discussion of the effects on alloys we have seen that some of the effects are caused only when interstitials and vacancies are mobile, and in the section on effects on the resistance of pure metals we saw that the effects were more pronounced when irradiation was carried out below room temperature, implying that the damage caused by a low temperature bombardment had appreciably annealed before room temperature. In this section we shall consider those experiments designed to investigate the kinetics of this recovery. Before proceeding to discuss the individual experiments, it is probably desirable to examine briefly the model of thermally activated recovery kinetics in terms of which most of the data are analysed. If the resistivity is due in part to some defect which is capable of annealing out, and if the resistivity of each defect is always the same, then the annealing of the resistivity will obey the same equations as the annealing of the number of defects. Further if the defects anneal by migration through the lattice to some sort of sink, and if each move in the migration requires a certain activation energy $Q$, then the equations governing the annealing will be the familiar equations for first or second order chemical reactions if the defects are at first randomly distributed, and some other simple law if the distribution is capable of mathematical simplification. In particular, if the first order chemical rate process is appropriate then the rate of loss of defects is

$$\dot{n}=-(n\nu/x)\exp(-Q/RT), \qquad \text{(1)}$$

where $n$ is the number of defects, $x$ the number of jumps before meeting a sink, $\nu$ the atomic frequency, $Q$ the activation energy and $T$ the absolute temperature. A similar expression with $n^2$ instead of $n$ occurs if the process is second order. In either case the activation energy can be found by changing the temperature, and then solving the equations for the rate immediately before and after the change, thus if $R$ is the ratio of the rates after and before changing from temperature $T$ to temperature $T'$ then

$$Q=TT'\log R/(T'-T). \qquad \text{(2)}$$

This procedure is perfectly valid if $Q$ is not a function of $T$, even if it is a function of $n$. In practice, however, we are probably not dealing with a simple process, except under certain very special conditions, and in particular if an analysis such as that we have been discussing shows that $Q$ is a function of temperature, then this could mean either that one process is occurring whose activation energy does vary with temperature, or that a series of different processes are occurring simultaneously. The former situation can be adjusted by solving the differential equation

$$RT^2\frac{d}{dT}(\log\dot{n})=Q-T\frac{dQ}{dT}; \qquad \text{(3)}$$

but the second, and probably more likely case cannot be dealt with so easily, as the state of annealing of all the different processes will be a function of the temperature history of the sample, and so no simple annealing kinetics will suffice. It is normal in this case to assume that all the processes with activation energies below a certain value will anneal very rapidly during an isothermal anneal, while those with activation energies above this value will effectively not anneal at all, and that the annealing observed at any temperature can thus be regarded as due to a fairly narrow band of activation energies, whose centre is given by eqn. (2). However, too much reliance should not be placed on these results until the underlying assumptions have been confirmed and the corresponding theory worked out. With this warning, we now turn to the experimental results.

Dugdale (1952, 1955) has studied the annealing of the additional resistance caused by both pile irradiation and cold work in platinum. The irradiated specimens were kept in the Harwell pile, BEPO, at about 50°c, for a thermal neutron flux of about $4\times10^{18}$ nvt, after which time their resistance, measured at the triple point of water, had increased by 0·3%. Of this increase about 15% was annealed out by two anneals one at 70°c for 646 hours, the other at 90°c for 336 hours. The annealing curves allowed the activation energy to be calculated, and a value of 1·19 ev was obtained in excellent agreement with the value of 1·20 ev obtained in an exactly similar test on a specimen whose resistivity had been increased 1·5% by cold work. This is strong evidence for the same mechanism being responsible in the two cases. More recent work by Kinchin (reported in Dugdale 1955) has extended this study to tungsten and molybdenum. In tungsten 20% of the additional resistivity anneals between 70° and 270°c with an activation energy that varies from 1·2 to 1·6 ev, while in molybdenum 60% of the additional resistivity anneals between 100° and 160°c with an activation energy that varies between 1·25 and 1·35 ev, and 30% anneals between 190° and 270°c with an activation energy of 1·46 ev. Stored energy measurements are also being made on molybdenum samples.

The majority of the work on the annealing of radiation induced resistivity has been done on the noble metals, and in particular on copper. Marx, Cooper and Henderson (1952), Henderson, Cooper and Marx (1952) and Marx, Koehler and Wert (1952) reported the first studies of low temperature bombardment of copper, silver and gold and also of nickel and tantalum; they measured the resistivity changes on deuteron bombardment at −140° and −150°c, and found increases which confirmed the theoretically expected dependence on atomic number and binding, and also found that the effects at the two temperatures were not the same but that recovery appeared to be taking place at these temperatures with an activation energy of about 0·2 ev. Their other observations have now been largely superseded by the later experiment of Cooper, Koehler and Marx (1955), and so will not be further discussed.

The annealing of radiation damage in copper has been studied systematically by Eggleston (1953 a, b) and Overhauser (1953 a, b, 1954) Eggleston has used a pulse annealing technique to study the recovery of the residual resistivity of copper after bombardment at −150°c with alpha particles. He obtained an activation energy of 0·717 ev for annealing between −65° and −20°c. A third order reaction was needed to fit the data in this temperature range. He also found that for annealing at temperatures between 250° and 325°C, the activation energy was 2·12 ev and a fourth order reaction was required. He also compared the annealing of resistivity of the radiation damaged copper with that of copper wires cold worked in liquid helium. Up to about −80°C the rates of annealing were similar, but above this temperature the radiation damage annealed more rapidly than the cold work. This could be attributed either to resistivity caused by dislocations in the cold-worked case, or to the fact that vacancies and interstitials are clustered in the radiation damage case and hence anneal more easily than the rather evenly distributed damage in the cold-worked metal.

At this point it may be noted that McReynolds *et al.* (1954, 1955) have studied the annealing of both the additional resistivity and the critical shear stress of copper and aluminium after low temperature neutron bombardment. The increased resistivity partly annealed between −80° and +20°C with an activation energy of 0·6 ev while the critical shear stress remained unchanged, but the remaining resistance change and the critical shear stress annealed between 300° and 400°C with an activation energy of 2 ev. In aluminium both properties annealed together between −80° and −20°C with an activation energy of 0·55 ev in a second order process.

Overhauser (1953 a, b) has bombarded copper wires with 12 MEV deuterons at −180°C and studied the recovery during isothermal anneals at temperatures from −185° to +167°C. He measured the resistance very accurately, and reports that the additional resistance, $r$, caused by irradiation is independent of temperature, or at least that if $r=r_0(1+aT)$, then $a$ is less than 0·0002. This seems to be in conflict with the results of Bowen and Rodeback (1953 a, b) reported in § 5. A direct comparison of the two experiments is difficult, both because of the different temperature ranges employed, and because of the lack of detail on the experiments in Bowen and Rodeback's report, but it seems improbable that the temperature dependent resistivity should only be affected at low temperatures.

Overhauser's main experimental results concern the annealing kinetics. He finds that the annealing, even at −185°C, is sufficient to account for most, if not all, of the falling off of the resistivity-flux curve, and that the recovery at these low temperatures and up to −60°C cannot be accounted for by a process with a single activation energy, but that the apparent activation energy is approximately proportional to the absolute temperature, being 0·44 ev at −100°C. This result needs further consideration, as Overhauser used eqn. (2) to deduce the activation energy, and as stated above, this procedure is valid only if the activation energy is not a function of temperature. In fact if the activation energy were proportional to temperature then substitution in eqn. (1) shows that the rate of the process would be independent of temperature, which it certainly was not. If the process is assumed to be a single one with a variable activation energy, then Overhauser's results can be interpreted as meaning that the left hand side of eqn. (3) is proportional to temperature, and the resulting differential equation can be solved to give

$$Q = BT \log T + CT,$$

where $B$ and $C$ are constants, and this in turn implies that

$$\frac{d\rho}{dt} = AT^{30},$$

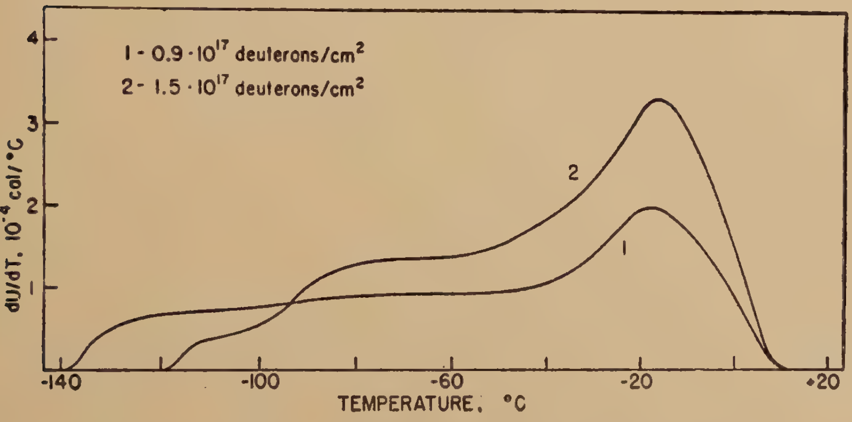
if the slope of Overhauser's experimental straight line is used. At this stage it is clear that the whole activation energy concept is of little value. In fact it seems more likely, not that the activation energy of a single process is varying, but that we are dealing with a large number of superimposed processes, and in this case if the processes largely involved at the two temperatures used to determine $Q$ are different, then it may not be the activation energy that is important in determining the annealing rates, but the numbers of defects involved in the two processes. What is certain is that below −100°c the annealing of radiation damage does not follow a simple activation law, or any small number of such laws. About one half of the additional resistivity anneals in this range.

Above −60°c and up to room temperature the recovery can be described by a single activation energy of 0·68±0·02 ev, in good agreement with Eggleston's observations, and this process accounts for a quarter of the additional resistivity. The remaining quarter did not anneal out in the temperature range studied. The order of this reaction was 2·5, whereas one would hardly expect the process to be of order higher than 2. This agrees, however, with Eggleston's observations and is attributed by Overhauser to the effect of lattice strains. Marx (1953, see also Koehler 1953) has pointed out that it could be due to the clustering of defects. This would produce a reaction of apparently higher order than the same process for initially homogeneously distributed defects. Dienes (1953 c) has suggested another possible explanation. If the activation energy is a linearly decreasing function of the number of defects present, then the annealing curves will be similar to those for a process with a constant activation energy but a higher order. Unfortunately, the stage to which annealing has proceeded by a given temperature is always about the same in these pulse-annealing experiments, and so it is uncertain whether the activation is constant during annealing at a given temperature, and it seems more probable that it is not.

Overhauser interpreted these results as follows. The low temperature annealing is due to interstitial and vacancy pairs recombining, the variable activation energy being due to variable initial separation. The recovery process above −40°c is due to volume diffusion of vacancies and their annihilation with interstitial atoms, in a second order rate process if the concentration is low, but with deviations from the usual equation due to the lattice strains round interstitial atoms if the concentration is high. If this interpretation is correct (as seemed reasonable since activation energies of the same order have been found in quenched and cold worked metal as will be again mentioned below), then self diffusion measurements, which give the sum of activation energies for formation and movement, can be split down to give the activation energy for vacancy formation as 1·39 ev, comparable with the calculated value of about 1·5 ev. However further work, to be described below, casts doubt on this assumption.

In later work, Overhauser (1954) measured the energy released when irradiated copper was warmed from −150°c to room temperature after a bombardment of $0{\cdot}9\times10^{17}$ deuterons per cm$^2$ at 12 mev. He obtained these data by a very delicate measurement of the temperatures of an irradiated and an unirradiated sample and an enclosure when the two samples were simultaneously warmed at symmetrical points in the enclosure. In this way he was able to deduce the rate of energy release with temperature. The resulting curves are shown in fig. 3. The total heat released up to room temperature was about 0·05 cal per g. As the energy of a vacancy interstitial pair has been calculated by Huntington (1953) to be 5 ev, which can hardly be wrong by more than a factor 2, this experiment gives an estimate of the number of pairs present in the material after bombardment as $5\times10^{-5}$, compared with $2{\cdot}5\times10^{-3}$ calculated on Seitz's theory using Eggen and Laubenstein's value for the displacement energy. As Overhauser measured the resistance changes simultaneously, he could relate the energy released to the resistivity lost, and so obtained a value of $1{\cdot}7\pm0{\cdot}2$ cal per g per micro ohm cm. This can be used to obtain an experimental value of the resistivity of a pair of defects using Huntington's energy of formation. This gives 11 micro ohm cm for one atomic % of defect pairs. This is to be compared with the calculated value (Jongenburger 1953, Abelès 1953, Blatt 1955) of about 2·7. This discrepancy of a factor four is more likely to be in the calculation of resistivity

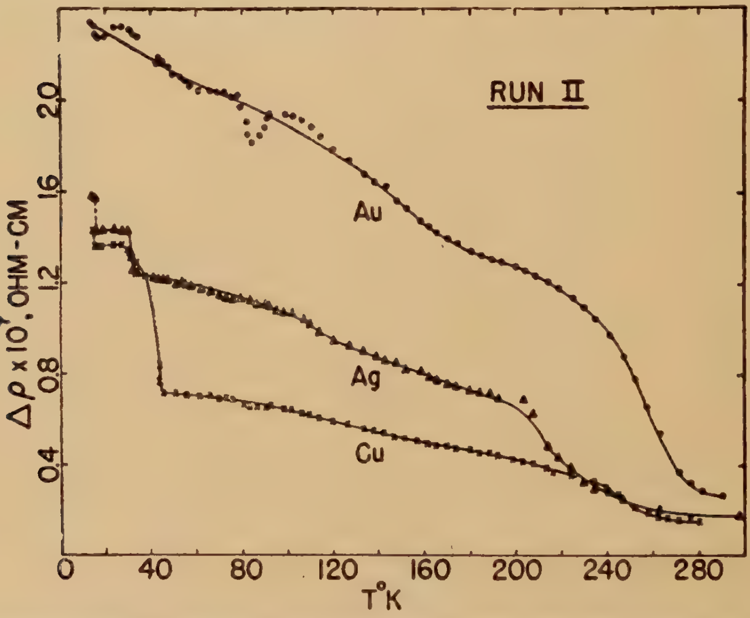
Fig. 3



The stored energy released during the annealing of two irradiated copper samples, each weighing 0·219 g. (Overhauser 1954.)

than in that of the formation energy of the defects, although Blatt, Huse and Rubenstein (1955) point out that the calculations of the resistivity caused by small concentrations of gallium, germanium and arsenic in copper give values twice those observed and that the theory in this case gave discrepancies of the opposite sign to those deduced here. Overhauser (see Koehler 1953) has also calculated the energy needed to anneal close vacancy interstitial pairs adjusting his parameters to give an activation for vacancy diffusion of 0·68 ev. The various geometrical locations give energies of 0·20, 0·32, 0·42, 0·46, 0·50 and other higher energies in electron volts. It is suggested that very low temperature annealing of irradiation damage may be able to pick out the lowest of these.

Fig. 4



Thermal recovery of copper, silver and gold specimens irradiated near 10°K. (Cooper, Koehler and Marx 1955.)

It is perhaps of interest to record here that Hoffman and Rasor (1954) and Rasor (1955) have reported finding similar annealing effects in copper films deposited *in vacuo* on glass at temperatures from −150° to −100°C. In this case the resistivity difference was much larger (~700% of the annealed resistivity), but the phenomenologically determined activation energies were similar.

Cooper, Koehler and Marx (1954, 1955) have bombarded copper, silver and gold near 10°K, as has already been mentioned in § 5 above. They found no annealing when the specimens were left at the bombardment temperature for some time, and, on annealing the resistivity of copper and silver (but not gold) showed abrupt drops at 40°K (−233°C) and 30°K (−243°C) respectively, as shown in fig. 4. They suggest that this might be due to the recombination of the close vacancy–interstitial pairs, although they point out that interstitial migration might require only 0·07 ev and so might be entering here. The total deuteron flux used by Cooper, Koehler and Marx is practically the same as that used by Overhauser (1953 a, b, 1954), and it is of interest that the additional resistivity left in Cooper, Koehler and Marx's specimens when they had reached 90°K was about $1\times10^{-7}$ ohm cm whereas Overhauser's observed resistivity change was $0{\cdot}7\times10^{-7}$ ohm cm. This means that the results of the two experiments are probably strictly comparable, and further that at these temperatures the effect of low temperature bombardment followed by an anneal is much the same as the effect of a 'high' temperature bombardment. Overhauser found that the ratio of stored energy released to resistivity annealed was the same in the two annealing stages he followed. If a similar ratio is assumed to hold in the lower temperature annealing, then Overhauser's results can be extrapolated to these temperatures, and for example, the number of defects induced at 10°K can be found. As about 55% of the resistivity increase annealed between 10°K and 90°K, the amount of damage in these specimens is about 2·6 times as much as that which annealed in Overhauser's experiments, i.e. about $1{\cdot}3\times10^{-4}$ of the total atoms displaced, compared with the figure of $2{\cdot}5\times10^{-3}$ calculated on the Seitz theory, using Eggen and Laubenstein's displacement energy, which, as it was determined at liquid air temperature, may be too high a value—allowing for which would make the agreement even worse. This discrepancy is discussed further in § 14.3.

The interpretation of these experiments has been further discussed by Brinkman, Dixon and Meechan (1953, 1954). The annealing observed at about −30°C appears to be a well-defined phenomenon, associated with the movement of a definite defect, probably either a vacancy or an interstitial. To decide which, Brinkman, Dixon and Meechan call on the evidence of the annealing of the additional resistivity caused by cold work in copper. If it is assumed that cold work also produces both interstitials and vacancies, but that unlike irradiation it produces many more vacancies than interstitials, then it would seem that the annealing in cold worked copper at −30°C observed by Eggleston (1952) is due to the same defect as causes the annealing in irradiated copper, and that the annealing observed between 100° and 200°C (Bowen, Eggleston and Kropschot 1952) is due to the annealing of some defect not present in any quantity in irradiated copper when it reaches these temperatures, as no annealing is observed in this case. Now Brinkman, Dixon and Meechan point out that the annealing of this process, at least in its earlier stages, has kinetics much more like those of a point defect migrating to some boundary sink than those of a chemical rate equation, thus for example it has an infinite initial slope, and they suggest that this points strongly towards this process being due to a point defect migrating to grain boundaries or edge dislocations. If both the annealing processes (at −30° and around 150°c) are due to point defects, then the low temperature one must be due to interstitials, as only in this way can one explain why the upper temperature one appears in cold worked but not in irradiated specimens—the interstitials remove almost all the vacancies in the irradiation case, but are not sufficiently numerous to do so in the cold worked material.

Having reached this conclusion, Brinkman, Dixon and Meechan point out that the activation energies for the two processes in pure copper (0·7 ev and 1·2 ev) are practically the same as those deduced for the case of $Cu_3Au$, and that the interpretation could in fact have been made on the basis of an analogy between the two materials.

This scheme however would predict that the lower annealing stage should not exist in quenched copper, as there should not be any interstitials present in this case, and as the experiments of Manintveld (1952) have shown that the annealing stages of cold worked copper and gold are extremely similar, the experiments of Kauffman and Koehler (1952, 1955) on the annealing of quenched gold are relevant. Kauffman and Koehler found annealing below room temperature, and deduced an activation energy of 0·68 ev from it. This they attributed to vacancy migration, and as their experiments on quenching from different temperatures gave an activation energy for vacancy formation of 1·28 ev, this assignment seems very reasonable, for the sum of these two activation energies should be the observed activation energy for self-diffusion, which is 1·965 ev and so a check on the values is obtained.

To explain this result on the scheme of Dixon, Brinkman and Meechan it would be necessary to say either that copper and gold are not similar (which seems unlikely) or that the annealing process is due to some other defect—either interstitials or bivacancies—present in the quenched material, but bivacancies, if present, should be capable of producing ordering in $Cu_3Au$, which, on the Brinkman, Dixon and Meechan scheme is similar.

There is thus a serious discrepancy in the scheme if the Kauffman and Koehler experiment is reliable, and it seems most desirable that it should be repeated on copper, so as to eliminate the difficulty of intercomparison between different metals. Meechan and Eggleston (1954) have made an experiment which gives a rather different result from that found by Kauffman and Koehler (1955). They measured the resistivity of both copper and gold at various temperatures, and assumed that the deviations from a parabolic law were due to the presence of vacancies. In this way they deduced values for the formation energies of vacancies in copper and gold (0·90±0·05 and 0·67±0·07 ev respectively), and hence using the activation energies for self-diffusion deduced the activation energy for vacancy migration to be 1·17 ev in copper and 1·54 ev in gold. These results would fit the scheme of Dixon, Brinkman and Meechan very well, but the experimental method would seem to be less direct than that of Kauffman and Koehler, and it is far from certain that the resistivity–temperature curve of the metal in the absence of vacancies would not have higher order terms than the second, as is assumed by Meechan and Eggleston.

A further difficulty in the scheme of Dixon, Brinkman and Meechan arises from the very fact that it supposes that copper and $Cu_3Au$ behave similarly. Recent experiments on threshold energies for producing effects in electron bombardment have shown that in copper the displacement energy is 25 ev (Eggen and Laubenstein 1953), while in $Cu_3Au$ it is below 13·5 ev (Dugdale 1955), and with differences as large as this in the displacement energy, it does not seem very likely that the other energies would be practically the same in the two materials. However, until further work has been done on the annealing kinetics, particularly of quenched copper and $Cu_3Au$, the various points raised cannot be solved. If the two materials are different, then the 0·7 ev activation energy in copper may well be vacancy migration, although the 1·2 ev process has to be explained. It has been found in cold worked copper (Bowen, Eggleston and Kropschot 1952, Smart, Smith and Phillips 1941) and gold (Meechan and Dieckamp 1955), but not in the quenched case as yet, and so it remains possible that it is something to do with dislocations, although it is difficult to see quite what is occurring especially if the kinetics are those of point defects migrating three-dimensionally to a sink, as suggested by Brinkman, Dixon and Meechan. If it should turn out that the 1·2 ev process is vacancy migration, then the 0·7 ev process in quenched material would have to be ascribed to bivacancies, which according to the calculation of Bartlett and Dienes (1953) should be much more mobile than single vacancies. Their detailed calculation may however be in error; Lomer (private communication) has pointed out that it essentially assumes a hexagonal close packed structure, in that atoms are assumed not to move out of the lattice plane, and also that its treatment of second-nearest neighbour forces is open to some doubt.

Throughout this discussion we have focused attention on the activation energies deduced from the various annealing experiments. The experiments can yield further data, however, some of the most interesting of which concern the time taken to produce the annealing (an approach suggested by Koehler 1954). Lomer and Cottrell (1955) have pointed out that, knowing the activation energy and assuming a vibration frequency, one can deduce from the annealing data the average number of jumps a defect makes before it is annihilated. If this is done, a rather curious result is obtained. At temperatures below $-100°$c the number of jumps so deduced is about $10^8$, while above $-60°$c it is about 10. If a reasonable number of vacancies and interstitials were present, one would have expected a figure of about $10^4$, possibly rising somewhat with temperature as the number of traps decreases. There is therefore both an anomalously large number of jumps at low temperatures, and an anomalously small number at high temperatures.

Lomer and Cottrell have considered various possible explanations of these anomalies. At high temperatures the observed effect would be obtained if the defects concerned in this range were not free to move about the lattice, but were trapped in the neighbourhood of impurity atoms. The activation energy for annealing would not then be the activation for diffusion of the defect, but the sum of this and another activation energy for escape from the neighbourhood of the impurity atom. Once the defect had escaped it could quickly diffuse to a sink, as thermal activation would be much greater than the energy required for diffusion alone, and thus an anomalously low number of jumps would be obtained by the simple calculation.

This explanation seems to fit the facts very well, but it must be observed that the activation energy so obtained if the defects were vacancies would not be the energy for diffusion of a free vacancy, and so should not be equal to the difference between the activation energies for self-diffusion and vacancy formation. As Kauffman and Koehler (1955) measured both this energy and the energy for formation in their quenching experiment, and as the sum of these gave the self-diffusion activation energy, this explanation cannot apply there, if this experiment and not that of Meechan and Eggleston (1954) is giving the correct value for the vacancy formation energy. A further outcome of the theory that might be open to experimental test is that the activation energy for annealing may well depend on what impurities are present in concentrations of about 1 : $10^4$, which may explain the variations sometimes observed from one laboratory to another.

In order to offer an explanation for the very large number of jumps at low temperatures, Lomer and Cottrell assume that the interstitials cannot wander through the lattice in three dimensions, but are restricted to a line. The figure of $10^8$ would then be of the right order to agree with a concentration of $10^{-4}$ vacancies per lattice point. Such a linear movement of interstitials could be necessary if the interstitial were situated not at the centre of the lattice cube, but in a close packed row, the strain being taken up by compressing the atoms along one close packed direction, thus forming a defect called a *caterpillar* by Frenkel and Kontorova (1939) and a *crowdion* by Paneth (1950). This form of defect could only move along the close packed direction in which the strain was relaxed, and would thus explain all the results. It is not as yet known, however, whether such a crowdion is stable; the only calculation that has been made is of its length, which has been studied by Fues and Stumpf (1955).

Having reached this stage, there obviously emerge other possible forms of annealing in radiation damaged solids. Thus a crowdion might well be trapped in the vicinity of a vacancy which lies a short distance away from its line, and, while unable to annihilate with it at the temperature for crowdion movement, the vacancy could move in when the temperature is raised enough to allow vacancy diffusion (or perhaps a little before). and annihilate the crowdion. This process will also require the vacancy to make very few jumps, and can thus provide a second explanation of the small jump number at high temperature for the radiation damaged case (though not, of course, for the quenched case).

Table 1. Activation Energies and Annealing Temperatures found in Copper, Silver, and Gold and their Alloys

| Material | Treatment | Activation Energy (ev) | Annealing Temperature Range (°c) | Reference |
|---|---|---|---|---|
| Cu<br>Ag | deuteron bombardment | 0·1 to 0·2 | −233<br>−243 | Cooper, Koehler and Marx (1955) |
| Cu | deuteron bbt. | varies with $T$ | −165 to −60 | Overhauser (1953 a, b) |
| Cu | cold work | scatter | < −140 | Eggleston (1952) |
| Cu | cold work | 0·44 | −140 to −70 | Eggleston (1952) |
| Cu | cold work | 0·20 | −150 to −50 | Manintveld (1952) |
| Ag | cold work | 0·18 | −150 to −80 | Manintveld (1952) |
| Au | cold work | 0·29 | −150 to −50 | Manintveld (1952) |
| Cu | deuteron bbt. | 0·68 | −60 to 170 | Overhauser (1953 a, b) |
| Cu | alpha bbt. | 0·72 | −65 to −20 | Eggleston (1953 b) |
| Cu | neutron bbt. | 0·6 | −80 to 20 | McReynolds *et al.* (1955) |
| Cu | cold work | 0·67 | −70 to 20 | Eggleston (1952) |
| Cu | cold work | 0·88 | −50 to 50 | Manintveld (1952) |
| Ag | cold work | 0·65 | −80 to 0 | Manintveld (1952) |
| Au | cold work | 0·69 | −50 to 50 | Manintveld (1952) |
| Au | quench | 0·68 | −30 to 15 | Kauffman and Koehler (1955) |
| $Cu_3Au$ | proton bbt. | — | −60 to 0 | Brinkman *et al.* (1954) |
| Ag–Zn | quench | 0·8 | 40 to 80 | Roswell and Nowick (1953) |
| Cu | cold work | 1 | 80 to 200 | Smart, Smith and Phillips (1941) |
| Cu | cold work | 1·23 | 100 to 250 | Bowen *et al.* (1952) |
| Cu | High $T$ resistivity | 1·17 deduced | — | Meechan and Eggleston (1954) |
| Au | cold work | 1·29 | 150 to 200 | Meechan and Dieckamp (1955) |
| Au | High $T$ resistivity | 1·54 deduced | — | Meechan and Eggleston (1954) |
| $Cu_3Au$ | electron bbt, cold work or quench | 0·9 | 100 to 130 | Adam, Green and Dugdale (1953)<br>Dugdale and Green (1954)<br>Brinkman *et al.* (1954) |
| Ag–Zn | quench | 1·1 | 40 to 80 | Roswell and Nowick (1953) |
| Cu | alpha bbt. | 2·12 | 250 to 325 | Eggleston (1953 b) |
| Cu | neutron bbt. | 2 | ∼ 320 | McReynolds *et al.* (1955) |
| Cu | self-diffusion | 2·05 | — | Maier and Nelson (1942) |

Table 2. Schemes that have been Proposed to Account for the Annealing in Copper

| Energy ev | Temperature °c | Broom (1954) | Brinkman *et al.* (1954) | Seeger (1955) | Lomer and Cottrell (1955) | |
|---|---|---|---|---|---|---|
| | | | | | Scheme I | Scheme II |
| 0·1–0·2 | −233 | Interstitial migration | Annihilation of close pairs | Annealing of melt zones | Interstitial migration | Crowdion migration |
| variation 0·2–0·5 | −160 to - 60 | Vacancy cluster migration | Annihilation of close pairs | Vacancy cluster migration | Release of trapped interstitials | Release of trapped crowdions |
| 0·7 | −60 to 50 | Vacancy migration | Interstitial migration | Interstitial migration | Release of trapped interstitials | Vacancy diffusion to crowdions |
| 1·2 | 100 | — | Vacancy migration | Vacancy migration | Vacancy migration | — |
| 2·1 | 320 | Self-diffusion | Self-diffusion | Self-diffusion | Self-diffusion | Self-diffusion |

In this table the names at the heads of the columns are intended to indicate only that the salient features of the schemes below are to be found in the papers indicated, only in the case of Seeger (1955) is a full scheme tabulated in the paper concerned, and details of the schemes here may differ from the current view of the author named.

Vacancies very close to crowdions might be able to move in with activation energies below those for ordinary vacancy diffusion, and might provide an alternative explanation of the variable activation energy region were the 0·2 ev activation to be associated with crowdion movement and the 0·7 ev activation to vacancy migration. It might be thought that the order of the reaction could help differentiate between these various possibilities, as annihilation of close pairs and of vacancy–crowdion systems are monomolecular processes, whereas interstitial, crowdion and vacancy migration and annihilation are bimolecular. However the clustered nature of radiation damage usually precludes this possibility, giving anomalously high apparent orders (Eggleston 1953 a, b). Perhaps electron damaged specimens may be free from this difficulty.

It might also be possible to account for the small jump number at high temperatures if vacancies come together to form bivacancies which then have a much lower activation energy.

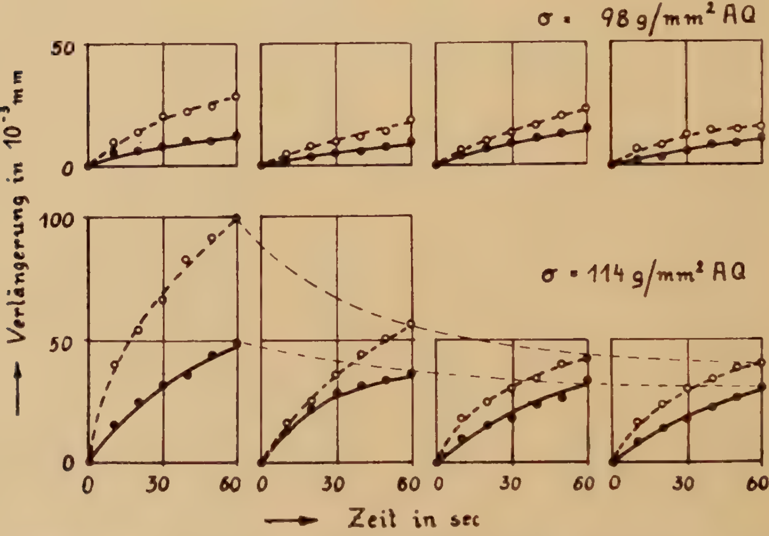
At the present it is therefore not possible to say which process is responsible for the annealing at any stage, even in copper, the metal which has been most studied, and so the data are presented in the form of two tables, the first summarizing the activation energies and annealing temperatures found, and the second the schemes which have been proposed. For further discussion of this problem, the reader is referred to a paper by van Bueren (1955).

## § 8. RADIATION EFFECTS ON THE MECHANICAL PROPERTIES OF METALS

### 8.1. *Creep*

The first radiation effect on mechanical properties to be reported was that bombardment with polonium alpha particles increased the creep rate of cadmium single crystals. Andrade (1945, 1953) found that bringing a source up to a creeping crystal produced an immediate increase in the flow rate, the largest being a factor five. The effect was more marked if the source was brought up soon after the beginning of the test, i.e. while the crystal was in the decelerating, transient creep range. At a later stage of the creep curve no measurable effect was obtained. Andrade suggested that this effect might be due to alpha particles initiating glide planes, and that the later stages of creep were associated with further slip on existing planes and thus are uninfluenced by alpha bombardment. Unfortunately in none of his tests did he remove the source to test whether the creep returned to a lower rate; tests were interrupted owing to wartime difficulties. Recently Makin (1954, 1955) has attempted to repeat this experiment, but although a stronger polonium source was used ($5\times10^{8}$ $\alpha/\text{cm}^2$ sec cf. $1{\cdot}5\times10^{8}$ $\alpha/\text{cm}^2$ sec), no effects were observed. It was however noticed that bombardment for 1–2 hours before testing reduced the creep rate somewhat. A similar experiment by Schmid and Lintner (1954 a, b) using zinc single crystals showed that here polonium alpha particles gave a strengthening during creep. Their method of testing was to creep the crystal for one minute, remove the stress for three minutes, and then creep for one minute again, alternative creep curves being taken with the source in position. They found that the creep curves under irradiation were only about half as rapid as those without irradiation which preceded them (the factor would not be so striking if the subsequent unirradiated curve had been taken), as shown in fig. 5. This effect is very difficult to interpret, as the irradiation is slight (the sources were of less than 20 mc) and if the effect were due to the formation of a surface film, then no annealing would be expected before the next unirradiated test, though as can be seen in the figure, some annealing does appear to be occurring. One experiment with a neutron source (radon–beryllium) showed an opposite effect, viz. a slight increase (20%) in creep rate (fig. 6). It is to be hoped that these tests will be continued, including continuous tests in which sources are brought up and removed while the specimen is creeping (the method of test used by Makin). With these very low irradiations it is unlikely that a measurable bulk effect could be produced. Nabarro (1948) has estimated the creep to be expected in a solid due to the additional number of vacancies and interstitials resulting from intense neutron bombardment, and found it to be generally negligible. On polycrystalline specimens some tests have been reported ; Jones, Munro and Hancock (1951, 1954) have studied the creep of polycrystalline aluminium while it was undergoing

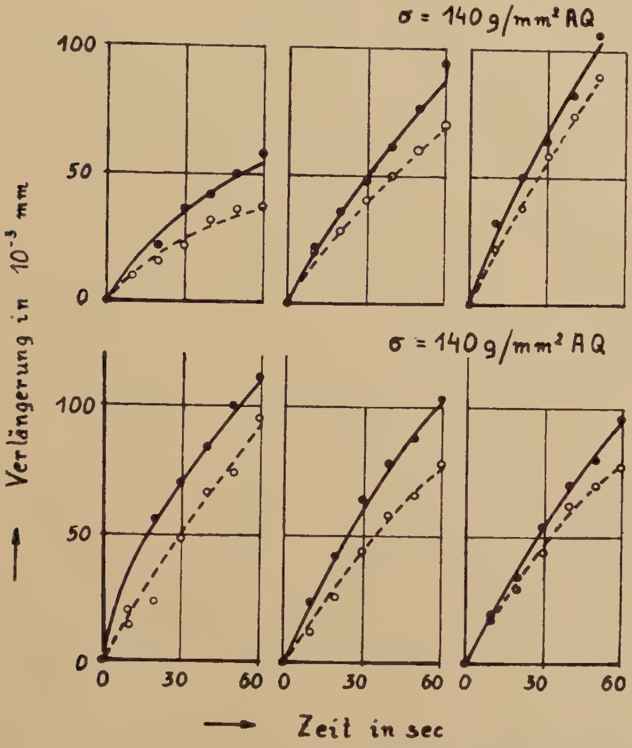
Fig. 5



Creep curves of zinc crystals with and without alpha irradiation. o – – – o : without, ●————● : with irradiation. The specimens were tested without irradiation for 1 min., rested for 3 min., tested with irradiation, rested for 3 min. etc. (Schmid and Lintner 1954 b.)

bombardment in the Canadian N.R.X. pile at a fast neutron flux of $1 \cdot 3 \times 10^{12}$ n/cm² sec. This experiment was performed by measuring the rate of radial expansion of a tube subjected to an internal pressure, the radial increase being measured by the pressure drop in air flowing through an annular gap round the tube. The results show that no large change in creep rate was caused by the irradiation.

Fig. 6



Creep curves of zinc crystals with and without neutron irradiation from a radon-beryllium source. o – – – o : without, ●————● : with irradiation. Method of testing as in fig. 5. (Schmid and Linter 1954 b.)

Another test on aluminium, this time in cyclotron bombardment, has been reported by Jeppson, Mather and Yockey (1954), Andrew, Jeppson, Mather and Yockey (1954), Jeppson, Andrew, Mather and Yockey (1955). They found no significant change during bombardment with $1 \cdot 2 \times 10^{13}$ $\alpha$/cm² sec. In fact both Jones *et al.* and Jeppson *et al.* found decreases in creep rate during bombardment which were within experimental error. Witzig (1951, 1952 a, b) has bombarded copper wire, 0·02 in. diameter, with deuterons from a cyclotron. He describes his experiments as being in the second stage of the creep curve, but from the curves he shows it is apparent that deceleration was occurring. No effect within the accuracy of the experiment (±20%) was observed, and as the rate of arrival of deuterons was $10^{12}$ cm$^{-2}$ sec$^{-1}$ and this gives an estimated vacancy concentration of 1 atom in $10^7$, this is not very surprising. An effect might be expected from the presence of thermal spikes, but here also the small volume over which the temperature is appreciably raised, and the small time for which such a rise lasts, is again sufficient to make it unlikely that a measurable effect will occur due to direct action of the radiation or its damage, as opposed to surface catalysis of the form suggested by Andrade.

Another reported experiment has been made at Purdue University. Preliminary reports of apparatus have been given by Gossick (1952) and Pizarro (1952, 1953), who plan to measure yield stress and Young's modulus of molybdenum and the creep of 0·3 mm diameter polycrystalline copper before and after deuteron bombardment. Preliminary results of the creep experiment show that for small fluxes no important change in creep rate is observed (Lark-Horovitz 1952).

### 8.2. *Hardness*

Perhaps the easiest mechanical property to measure is the indentation hardness, and several workers have used this to get some idea of the behaviour of metals after irradiation. Billington and Siegel (1950) investigated the effect of pile irradiation on the Rockwell F hardness of annealed and cold worked copper. For annealed copper the hardness went from $R_F43$ to $R_F90$, and for cold worked from $R_F93$ to $R_F97$. In copper–beryllium alloys the hardness changed together with the electrical resistance. Hardness increases were also observed in stainless steel, Monel, 65/35 brass and silicon bronze.

Geib and Grace (1952 a, b), Harmon, Eidam and Geib (1953), Harmon, Horvath and Geib (1953) have studied the effect of deuteron irradiation on the hardness of molybdenum, using a Knoop indenter with various loads. Despite a larger scatter of experimental results, part of which can be attributed to varying grain orientation and other eliminable causes, an increase of hardness can be observed on an annealed specimen. Later experiments with somewhat lower irradiations gave much smaller changes, and so this result is not to be given too much weight until further work has been done. A disturbing feature was the appearance, after irradiation, of an unidentified surface film which appeared to be removed with trichlorethylene, but which may be still exerting an influence on the hardness.

To avoid thermal spike effects, Dixon and Meechan (1953) have used 1 MEV electrons to bombard copper at −20°C. Tukon hardness measurements showed a rise from 44·3 to 47·7 VPN, about half of which annealed out in 8 hours at 170°, which can therefore, presumably, be attributed to a hardening caused solely by vacancies and interstitials.

Murray and Taylor (1952, 1953, 1954) whose results on the electrical resistance of copper–beryllium have been reported above, also found that the hardness of a large number of solid solution alloys increased by

10 to 20 VPN on irradiation while that of Cu–Be increases by ~40. This increase was not correlated with the resistance increases; this difference in the precipitation hardening alloys is attributed to the different sized particles needed for the two effects. Fillnow, Halteman and Mechlin (1953) have made Vickers hardness measurements on their $Cu_3Au$ specimens; disordered samples increased from 100 to 121 VPN and ordered from 110 to 158 VPN, the greater change being due presumably to further increases in order in the ordered specimen, a deduction confirmed by sharpening of the X-ray lines in this case.

### 8.3. *Stress–strain Curve: Single Crystals*

Blewitt and Coltman (1951) have investigated the effects of pile irradiation on the stress–strain curves of copper single crystals both at room temperature and liquid nitrogen temperature. The first tests showed that a specimen irradiated with a fast neutron flux of $1{\cdot}8\times10^{18}$ nvt and tested at room temperature had a critical shear stress of 1·94 kg $mm^{-2}$ compared with 0·24 kg $mm^{-2}$ for an unirradiated sample. Further tests by Jamison and Blewitt (1952, 1953 a) showed that the slip lines were more clustered in irradiated single crystals and more cross slip was observed than in unirradiated crystals, and a reduction of stress occurred when a new slip system was started; all these effects are similar to those observed in (unirradiated) alpha brass. When the testing temperature (but not the irradiation temperature) was lowered to 78°K the critical shear stress is further increased (although for unirradiated crystals it was independent of temperature), but the initial rate of work hardening was decreased so that the curve was indistinguishable from that of an unirradiated crystal after about 20% strain. Cross slip is not as distinct and the slip lines were more closely spaced and in smaller clusters than at room temperature. Some of the irradiated crystals broke brittly at 78°K after several audible clicks.

The recovery of the critical shear stress of copper crystals has been studied by Redman, Coltman and Blewitt (1953). They annealed specimens at a series of temperatures between 300° and 400°C. No recrystallization was observed although the critical shear stress had been raised from 0·2 to 3·5 kg $mm^{-2}$. The relaxation time for recovery of the critical shear stress varied from 400 hours at 305°C to 11 minutes at 385°C, and an activation energy of 2·2 ev was found, this energy is higher than those found for the recovery of electrical resistance, and is of the same order as that for self-diffusion, i.e. for the creation and movement of vacancies.

McReynolds, Augustyniak, McKeown and Rosenblatt (1954, 1955) have also studied the change of critical shear stress of copper and aluminium after intense neutron bombardment at below −150°C, and found changes of several hundred per cent. For copper they found that the change annealed at about 320°C, together with that part of the resistivity increase remaining after lower temperature annealing processes, while for aluminium both properties annealed in the range −80° to −20°C. The activation energies being about 2 ev and 0·55 ev respectively.

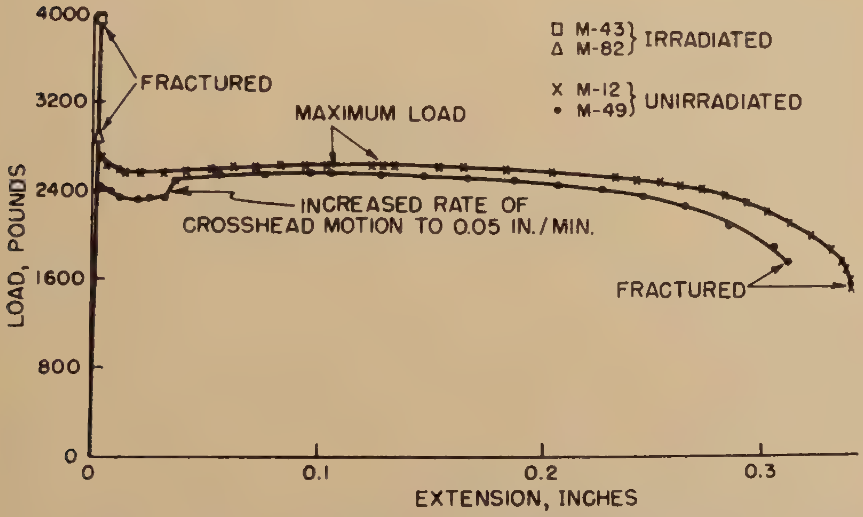
Kunz and Holden (1954 a, b) have also studied the effect of neutron irradiation on the stress–strain curves of single crystals. Their total flux was only a tenth of that used by McReynolds *et al.*, and their samples were irradiated at room temperature. It is therefore not surprising that no change was found for lead crystals ; the other samples, iron and zinc, showed marked changes. Annealing tests on the iron crystals at temperatures between 200° and 500°C gave an activation energy for recovery of the yield stress of 3·1 ev, that is to say of the same magnitude as the activation energy for self-diffusion. Holden and Kunz (1954), Kunz and Holden (1954 b) have suggested that, as the effect of the yield stress anneals only with the activation energy for self-diffusion, agglomeration of interstitials into stacking faults might be the dominant mechanism, but the X-ray evidence is difficult to interpret in this way ; so the agglomerations would have to be like Preston–Guinier zones. They suggest the following experiments may help solve this problem. (1) Irradiation at 78°K, which on their theory should give a smaller effect on the shear stress if the interstitials have not agglomerated (though, as we have seen, McReynolds *et al.* (1955) have found that the critical shear stress is, if anything, raised more at this temperature). (2) Measurement of the electrical resistivity parallel and perpendicular to the basal plane in hexagonal metals, as here agglomerates should form parallel to the basal plane, and hence give a different effect in the two directions. Holden and Kunz also point out that if Cottrell locking of dislocations by point defects is responsible, the damaged specimens should strain age.

Kelly (1954, 1955) has studied the effect of alpha bombardment at −100°C on the structure of slip bands in aluminium, as seen by the electron microscope. He found that specimens tested at −196°C showed an increase in the amount of slip on a given plane, as compared with unirradiated samples tested (in bending) to the same strain. Samples tested at room temperature showed no effect, hardly surprisingly in view of the annealing found by McReynolds *et al.*, while specimens tested at −78°C were rather inconclusive. An analogous result that can be quoted, is that Maddin and Cottrell (1955) found that quenched aluminium crystals show a greatly increased yield stress, reduced rate of work hardening and coarser slip bands than slowly cooled ones. This result can be attributed to the jogs produced by vacancies on dislocations, and occurs at room temperature, as in this case there are no interstitials to remove the vacancies in other ways. In the irradiation case the effect on critical shear stress may be caused in a similar way by those vacancies and interstitials which migrate to dislocations, though the annealing would seem to be different, and the arguments put forward by Kunz and Holden still need to be answered. If interstitials are mobile below liquid nitrogen temperature, then they may be responsible for the increase in yield stress observed at that temperature, or else the density of defects may be sufficient for the dislocations to pick up sufficient number for the yield stress to be raised without migration being necessary. At present, however, the actual mechanism of the hardening is still unknown, and more experiments are needed to distinguish between the various theories.

### 8.4. *Stress–strain Curve : Polycrystals*

One of the most marked effects of irradiation on mechanical properties is on the ductile-brittle transition. This phenomenon has been observed in molybdenum by Bruch, McHugh and Hockenbury (1954, 1955). Irradiation with neutrons to a dose of 1·9 to $5{\cdot}9\times10^{20}$ nvt raised the ductile-brittle transition from −30° to +70°C, and thus the effect on the room temperature stress–strain curve was most striking (fig. 7). Bruch *et al.* carried out tensile tests from 21·8°C to 100°C, and plotting the fracture stress against temperature showed that, while both the brittle strength curve and the plastic flow curve had been raised, the latter had been raised much further, causing the rise in transition temperature (fig. 8). As the microstructure had not changed during irradiation, Bruch *et al.* attributed the effect to the action of point defects.

Fig. 7

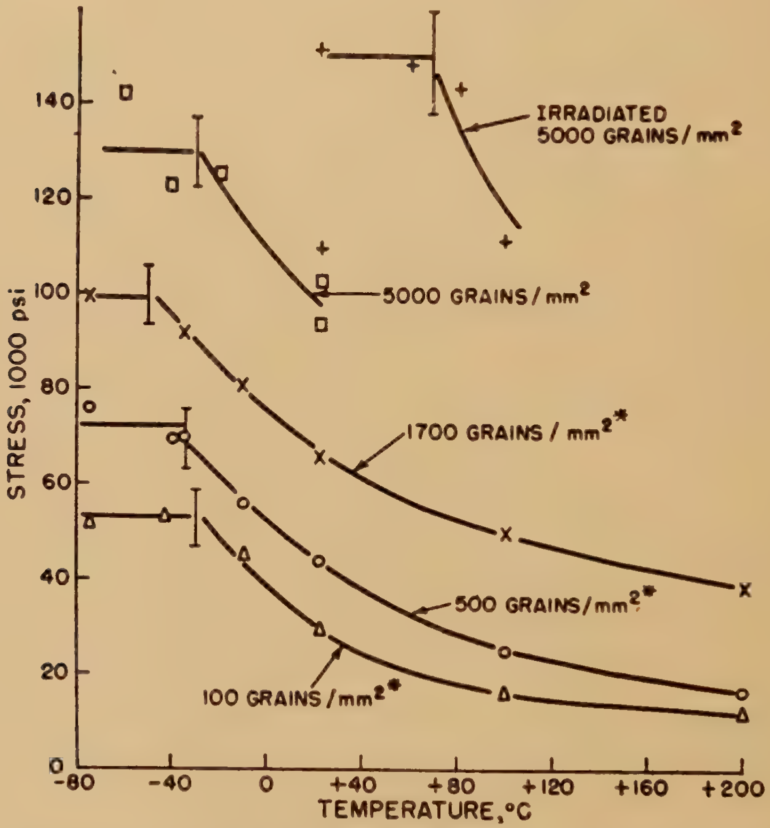


Load elongation curves of irradiated and unirradiated molybdenum at room temperature. (Bruch, McHugh and Hockenbury 1955.)

Makin (private communication) has tested various metals after pile irradiations of $5\times10^{19}$ nvt. He found that molybdenums showed a 4% increase in yield stress at room temperature and at 150°C, and that titanium showed a 15% increase when tested at liquid air temperature, dropping to about 7% at 200°C. In nickel, the effect was even larger;

the yield stress at 78°c was doubled, and that at 300°c was raised 35%. The ductility as measured by the extension decreased, as did the rate of hardening, so that the area under the stress–strain curve of nickel was not much affected. In copper similar results were observed. Annealing tests have been made on copper and nickel specimens, in copper the yield stress annealed between 300° and 360°c with an activation energy of 2·05 ev, while in nickel annealing occurred between 340° and 400°c with an activation energy of 2·63 ev. However, in this case some annealing appeared to occur between 100 and 300°c. The nickel annealing seems to occur much faster than the copper (~100 times) for the same exponential term. Experiments are proceeding to check this, and to study the effects of neutron dose and previous cold work. The tests are also to be extended to other metals.

Fig. 8



Yield and fracture stress as a function of grain size, neutron irradiation and temperature for molybdenum. Fracture stress curves are to the left of the vertical lines, and the flow stress curves to the right. (Bruch, McHugh and Hockenbury 1955.)

Meyer (1954) has studied the effect of deuteron bombardment on the notch sensitivity of mild steel, and found that the ductile-brittle transition was raised from −1° to 18°C, and was not a linear function of dose. The Knoop hardness was also raised, from 180 to 380. The annealing behaviour was different from that of workhardened specimens, and occurred between 260° and 480°C with a variable activation energy ; the effect of 5% cold work annealed between 315° and 371°C.

Steele and Wallace (1954) have studied the effect of neutron bombardment on the stress–strain curves of a series of aluminium alloys in the annealed, strain hardened and aged states. In general they found that both yield stresses and ultimate tensile strengths were raised, the magnitude of the increases being greatest in the annealed specimens, although the increases in the strain hardened alloys were sufficient to raise the tensile strength above the values obtained by optimum strain hardening. The ductilities were generally (but not always) decreased. The strain hardening exponent (i.e. the best power law fit to the true stress–true strain curve) was greater for the irradiated specimens, which agrees with earlier observations of increased yield stress but decreased hardening rates. A satisfactory feature of these experiments is that about 20 to 25 specimens were tested for each alloy in the irradiated condition, thus providing a check of the reproducibility of the results.

The effects of irradiation on a variety of structural materials have been reported by Sutton and Leeser (1954 a, b). They present tables showing the effect of doses up to about $3 \times 10^{20}$ nvt of thermal neutrons ($\sim 1 \times 10^{20}$ nvt fast neutrons) at temperatures from 20° to 250°C on the hardness of various steels, nickel and cobalt based alloys and zirconium, and on the ultimate tensile strength and ductility of the same materials and of tungsten, tantalum and some of their alloys. Other properties studied are the impact behaviour of some boiler steels, the density of steels and nickel and cobalt alloys, the magnetic susceptibility and electrical resistivity of steels. Their results show that softer materials show a greater hardening on irradiation than harder materials, and that the effect in steels is not a simple function of carbon content. The effects tended to saturate before full embrittlement had occurred. As in the other experiments mentioned above, the ductile-brittle transition was raised. Sutton and Leeser do not consider that the effects need cause designers any great concern, though they should be taken into account. The magnetic susceptibility measurements showed that there was some tendency towards phase transformation from austenitic to ferritic iron (this gave increases in susceptibility of up to 600% after $10^{19}$ nvt), but Sutton and Leeser do not think the amount transformed is sufficient to increase appreciably the corrosion susceptibility of the more common stainless steels.

Typical figures for the effects observed by Sutton and Leeser are percentage increases of, for *hardness*, carbon steels 40%, stainless steels

100%, nickel 140%, zirconium 100%; for *ultimate tensile strength*, carbon steels 10%, stainless steels 20%, nickel 40%, zirconium 5%; the *yield strengths* being raised about twice as much as the ultimate tensile strengths.

### 8.5. *Internal Friction*

Li and Nowick (1955) have looked for an effect of pile irradiation on the internal friction of an alloy of 17 atm % aluminium in copper. They found no effect, and as quenching the same alloy from a high temperature gave a marked effect on the relaxation time at temperatures between 114° and 162°C, they interpret their null result as showing that the vacancies induced by irradiation are largely removed by other defects mobile below room temperature. No other measurements of the internal friction of irradiated metals have been reported.

### 8.6. *Elastic Constants*

The effect of irradiation on elastic constants was the subject of theoretical calculations by Dienes (1952 a), who found that interstitials should have a far larger effect than vacancies. Although this calculation has been questioned subsequently (Nabarro 1952, Dienes 1952 b) it seems probable that interstitials should increase the bulk modulus by a much larger amount than the same number of vacancies would reduce it. In confirmation of this Dienes (1953 a) reported that preliminary results of Bowman and Tarpinian showed that the Young's modulus of copper increased by as much as 10% on cyclotron irradiation. A final report of this work is still awaited. In contrast to this result, Charlesby, Hancock and Sansom (1954, 1955) found no significant effect of pile irradiation on the elastic modulus of an austenitic steel in an ingenious experiment in which was a clock was irradiated, and Kunz and Holden (1954 a, b) report no change in the elastic constants of copper to within experimental error (~1%) after $2{\cdot}4\times 10^{18}$ nvt of pile bombardment. Both of these pile experiments were carried out at ambient pile temperature, and it is possible that the effect reported by Dienes was at a lower temperature.

Dieckamp and Crittenden (1954) have reported that the shear modulus of copper decreased by about 1·5% on irradiation with $9\times 10^{16}$ deuterons of 20 Mev at −175°C. Of this about one-third annealed at −125°, very little further recovery occurring at −75°C. The final two-thirds all recovered between −50° and +100°C. Dieckamp and Crittenden say that the shape of the shear modulus annealing temperature curve was such as to suggest that the low temperature recovery corresponded to the rearrangement of dislocations until those remaining are pinned down by vacancies or interstitials, and that the subsequent annealing depends on the interstitials moving and annihilating vacancies. This explanation assumes that the reduction in shear modulus is due to the production or freeing of dislocations, whereas point defects might by themselves be expected to reduce the shear modulus, and in this case the whole effect could be due to their disappearance. This latter explanation would seem to be favoured by a later experiment of Dieckamp (1955) in which 1 Mev electrons were the bombarding particles. Unfortunately a value for the shear modulus of the unirradiated specimen is lacking, but annealing gave the following changes: −196° to −50°c, a 4% increase; −25° to 50°c, no change; 75°c, a ½% decrease; 100° to 200°c, no change; 250° to 350°c, 2% decrease. The explanation of these effects is not obvious, but their correlation with the annealing of other properties in irradiated copper may help to throw light on the clustering and annihilation processes of the vacancies and interstitials which are presumably the only primary damage formed by 1 Mev electrons.

## § 9. RADIATION INDUCED PHASE CHANGES

In § 6 we have already discussed examples of situations in which the enhanced number of vacancies or interstitials formed during irradiation can facilitate an approach to phase equilibrium, and other cases in which disequilibrium can be induced. Other examples of these phenomena have been observed by studying properties other than electrical resistance.

Although grey tin is the stable phase at low temperatures, white tin is metastable. Fleeman (1953, 1954), Fleeman and Dienes (1955), have observed that samples of tin irradiated at liquid nitrogen temperature in the Brookhaven pile showed a greatly enhanced transformation rate on subsequent heating to −50·3°c. A dilatometer was used to measure the rate of transformation in unirradiated, irradiated and seeded samples. The irradiated material had a somewhat longer induction period than the seeded samples, and probably a slower transformation rate, but both these quantities were much more repeatable in the irradiated than in the seeded samples. X-ray studies showed that grey tin was not formed by the irradiation in detectable amounts (0·05%), and that therefore the effects of irradiation are presumably due to defects induced by the irradiation which on heating either act as nuclei for transformation or, by diffusing, help to form such nuclei.

The reversion of an alloy to its stable phase has been used by Denney (1953, 1954 a) to determine the threshold energy for damage. An alloy of 2·4% by weight of iron in copper gives an iron precipitate coherent with the face-centred cubic copper lattice, and ageing at an elevated temperature makes this precipitate grow. Upon transformation of this precipitate to the stable body-centred cubic form, the iron becomes ferromagnetic and thus the saturation magnetization provides a direct measure of the amount transformed. This transformation can be initiated by point defects introduced by bombardment, and thus by bombarding with electrons of varying energy Denney was able to deduce the threshold energy for the production of vacancies. This occurred at 0·45 Mev, which corresponds to a displacement energy of 23 ev if a copper atom is the one displaced as was at first assumed by Denney (1953). If however an iron atom is responsible then a value of 27 ev is obtained, and if either can cause the transformation, then the latter is the correct figure. In his final report, Denney (1954 a) advances reasons why iron should be the displaced atoms involved, and shows that the curve of magnetic intensity versus bombardment energy is of the same shape as that expected theoretically if each displacement causes 200 atoms to transform to the body-centred cubic lattice.

The same alloy has been used by Denney (1954 b) to test another fundamental postulate of radiation damage theory. If the precipitate is fully transformed to the ferromagnetic form, then no thermal or mechanical treatment will restore it to the paramagnetic form other than heating it above the two phase region. An alloy with its precipitate in this ferromagnetic state was irradiated with 9 MEV protons, and it was found that the amount of ferromagnetic precipitate decreased. This Denney interpreted as being due to local heating in a thermal spike, or perhaps rather a displacement spike, as it must cover the volume of the precipitate particle. This is therefore a demonstration of the existence of such spikes, unless some other explanation can be found. The phenomenon can, however, be explained by replacement collisions (Kinchin and Pease 1955 a, b) if a sufficient number of knocked on iron atoms replace copper atoms in the face-centred lattice.

Another example of a metal reverting to a stable form may be provided by the austenitic steels studied by Sutton and Leeser (1954 a, b) in the experiments described in § 8·4, where the magnetic susceptibility increased by up to 600%, indicating some conversion to the ferritic form.

## § 10. RADIATION EFFECTS ON X-RAY DIFFRACTION AND DENSITY

Any marked changes in the lattice caused by radiation should show effects on the x-ray diffraction pattern. Apart from the effects in superlattice alloys and the changes of phase that have been referred to above, effects have been sought in stable, pure materials. Thus Sidhu and Henry (1950) looked at powder patterns from beryllium, graphite, diamond and aluminium after neutron bombardment from a cyclotron Be($\alpha$, n) source. Marked changes in the patterns from some were found (it is not stated which).

Warren (1951, 1952, 1953, 1954) found no line broadening on cyclotron bombardment of copper or zirconium, or electron bombardment of germanium. A single crystal of aluminium also showed no measurable broadening after six months in the Hanford pile. Pile bombardment of Cu 2% Si gave no effect on integrated intensities, no peak shift and no broadening, but subsequent etching with any of three reagents tried gave very broad peaks, although the same reagents applied to unirradiated material gave no change.

Adam (reported by Dugdale 1955) found no change of lattice spacing to 1 : 20 000 and no line broadening in platinum whose resistivity had changed by 2%, but did get an observable increase in lattice spacing (1 : 10 000) in molybdenum powder at an irradiation at which bulk molybdenum had changed its resistivity by 12%. Kunz and Holden

(1954 a, b) have also reported line broadening in copper and magnesium and both line broadening and a shift in brass (it is not stated of what composition). Adam (private communication) has found a rather striking effect in the hexagonal alloy $WAl_5$. On irradiation this alloy showed an expansion of the lattice of about 0·1% in the $c$ direction, and a slight contraction in the $a$ direction. This is far larger than the changes of lattice parameter normally found in metals, and may be an indication that this alloy has some non-metallic features.

Tucker and Sampson (1954, 1955) have pointed out that x-ray lattice parameter measurements should be much more sensitive to the presence of interstitials than of vacancies, and calculate that one should be able to detect 0·01% of interstitials in this way. That no such change is present in some metals, as indicated above, is probably a very good indication that in these metals interstitials have already disappeared at the temperature of the experiment. This could therefore be a very valuable method of determining which annealing processes involve interstitials. The statement of Tucker and Sampson that their expectation of a sizeable effect is borne out by experiments on neutron irradiated materials therefore arouses interest.

McDonnell and Kierstead (1954) have studied the volume change of copper on deuteron irradiation. The latest form of their results, reported by Kierstead (1955) is that $1{\cdot}15\times10^{17}$ deuterons per cm² gave a volume increase at the temperature of liquid nitrogen of 0·034% when averaged over the deuterons' range. The annealing of this was as follows : 10·8% below −105°c, none between −105° and −25°c, 2·9% between −25° and 0°c, none between 0° and 190°c, 3·6% between 190° and 260°c, and 2·9% between this and 400°c. Even at 400°c some 80% of the effect remained. Bombarding at room temperature, however, produced only about a tenth of the effect the same bombardment would have produced if made at liquid nitrogen temperature and then followed by an anneal at room temperature. The magnitude of the effect at the lower temperature is equivalent to about one-tenth of an atomic volume expansion per displaced atom, if the number of displaced atoms is calculated on the Seitz theory. No change of lattice parameter to 0·02% was found (it is not stated at what temperature this observation was made).

## § 11. OTHER EFFECTS IN METALS

### 11.1. *Diffusion*

The additional vacancies and interstitials present in bombarded material might be expected to raise the diffusion coefficient. However direct measurement of diffusion effects is only practicable at temperatures at which the diffusion coefficient is reasonably large, and at such temperatures the natural vacancies present in thermal equilibrium are usually much more numerous than the additional number produced by bombardment. Lomer (1954) has calculated that there only exists a small temperature range around 450°K in which the effects will be observable in copper. Above 550°K the bombardment-induced vacancies will be altogether negligible in number, below 350°K the diffusion coefficient will be too small to be measured by normal means, even with the aid of the radiation-induced vacancies. In other materials the position is probably similar, and it is therefore not surprising that no large effects have been reported.

Johnson and Martin (1952) have used radioactive tracer techniques to measure the self-diffusion of silver with and without simultaneous bombardment with 110 MeV protons. No observable change was found in either single or polycrystalline samples. The experiments in the temperature range 600° to 900°C gave an activation energy of $1\cdot82\pm0\cdot03$ eV, and a value of $D_0$ of $0\cdot11\pm0\cdot05$ cm$^2$/sec.

An effect which might be described as diffusion is reported by Callendine, Ridolfo and Pool (1952). They found that cobalt which had been plated with a layer of gold and then placed between 0·18 in. carbon discs and irradiated in a reactor, showed signs of having diffused into the carbon, where a half-life suggestive of $^{60}$Co was found. They suggest that this ‘ diffusion ’ is a direct result of collisions knocking the cobalt through the gold layer.

The results reported in § 6 on copper–gold alloys can also be interpreted as a result of increasing the diffusion rate, and it seems that at such temperatures as were used in these tests, where the diffusion rate is far too small to be measured by conventional methods, the rate is in fact increased many times, in agreement with Lomer's theory.

### 11.2. *Thermoelectric Effect*

Andrew, Jeppson and Yockey (1952) have studied the effect of cyclotron alpha bombardment on the thermoelectric power of iron, constantan, chromel, alumel, platinum and platinum 10% rhodium. No change of e.m.f. of greater than $3\times10^{-7}$ volts per °C (the limit of measurement) was found. Temperatures up to 500°C were used. Another null result has been reported by Jamison and Blewitt (1953 b) who tested copper–constantan and iron–constantan couples in a liquid nitrogen bath in the Oak Ridge pile. No change in e.m.f. to 0·01 mV was found, the warm junction being in ice. Palladino (1954) also reports a null result, while emphasizing the practical difficulty that most sleeving materials suffer damage.

A positive result has been found by Andrew and Davidson (1953) after 10 MeV proton bombardment of iron and constantan wires, the wires being cooled to below 0°C during irradiation. After irradiation the wires were annealed at various temperatures and then had their thermal e.m.f. measured against an unirradiated section.

## § 12. RADIATION EFFECTS ON THE PROPERTIES OF SEMICONDUCTORS

### 12.1. *Electrical Effects*

Another field in which much work has been done on the effects produced by radiation is that of semiconductors. The results obtained are of use in interpreting the results of experiments on normal metals, and will therefore be discussed in some detail.

According to the electron theory of metals, the electrons in solids can be thought of as existing in the various bands of energy values, into which the atomic energy levels have widened. If there is a distinct energy gap known as the forbidden band between one band and the next, and if there are enough electrons completely to fill all energy bands, up to the lower band, then, at temperatures low enough for the gap to be large compared with $kT$, the material is an insulator.

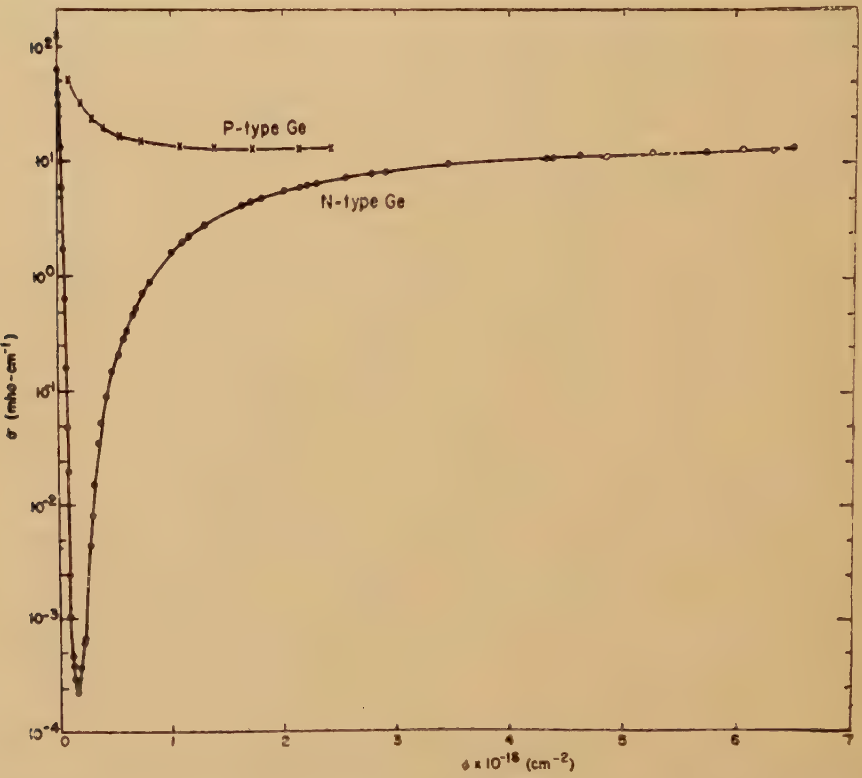
Semiconductors are materials in which, in the pure state, the above picture for insulators is true, but in which impurities or defects introduce other levels which allows some conduction to take place. Thus, for example, if an impurity atom with one more electron than the semiconductor atom is introduced, it will have one electron over and above those necessary to fill the band known as the full band, and this electron will be in an orbit round the impurity atom, a 'localized level'. Now it so happens that such a localized level is frequently only just below the bottom of the upper band, spoken of as the conduction band. In this case only a small activation is needed for this electron to get into the conduction band and give a small amount of conduction. Such a material is known as a n-type semiconductor; n-type because the electricity is carried by a negative carrier. The impurities are sometimes called donors.

Similarly, if an impurity atom has one electron less than a semiconductor atom, it can be thought of as providing a localized vacant energy level for an electron from the full band, which may be occupied by an electron from the full band with an energy much less than that needed for the electron to jump right up to the conduction band. If this level is so occupied, there is left a hole in the full band, and this hole behaves exactly like an electricity carrier of positive sign. Semiconductors of this sort are therefore called p-type. Impurity atoms of this type are called acceptors. The sign of the apparent electricity carriers can be determined by the sign of the Hall coefficient, the cross potential formed by a unit current flowing perpendicular to a magnetic field.

Impurities which introduce empty levels at the top of the forbidden band can remove electrons from the conduction band and those levels are called electron traps, while impurities which introduce full levels at the bottom of the forbidden band can give electrons into holes in the full band and are therefore called hole traps.

The usual way of preparing semiconductors is to have present a small number of impurity atoms which act as donors or acceptors for electrons, but vacant lattice sites or interstitials atoms can also act, and thus bombardment may be expected to affect the semiconducting properties. There are two other effects which bombardment can produce, which are, however, not of direct interest to us for comparison with the effects in metals which we are discussing. Transmutations can introduce new impurity atoms, but these, while radically affecting the semiconducting properties, are beyond the scope of this review; secondly transient effects can be produced due to the electron excitation produced by bombardment, but these effects have no analogue in metals. These effects must always be borne in mind when interpreting results of experiments. One fundamental difference is that the effects caused by vacancies and interstitials, while not transient in the sense that electronic excitation states are transient, can be removed by heat treatment, whereas transmutation effects obviously cannot. A full review of all the effects on bombardment on semiconductors up to 1950 has been written by Lark-Horovitz (1951).

Fig. 9



Change of conductivity of deuteron irradiated germanium as a function of dose. (Fan and Lark-Horovitz 1955.)

Early experiments (Lark-Horovitz, Bleuler, Davis and Tendam 1948) showed that when germanium of various types was bombarded with deuterons the resistivity of p-type and of pure germanium decreased, while n-type was converted to p-type, as though the primary effect was to introduce acceptor defects. The sort of results obtained are shown in fig. 9, which is taken from more recent work. Neutron irradiation gave the same result (Davis, Johnson, Lark-Horovitz and Siegel 1948, Johnson and Lark-Horovitz 1949), although only part of the neutron defects could be annealed at 400°c, the temperature at which the deuteron damage completely disappeared. The conductivity of n-type germanium showed a rapid decrease to a minimum followed by a much slower increase. When exposed, in cadmium shields the minimum occurred at a later stage than in graphite and heat treatment reproduced the original state. In contrast to these results on germanium; silicon, $Cu_2O$ and selenium semiconductors, irrespective of type, all showed an increase in resistivity on bombardment with both deuterons and neutrons, heat treatment again restoring the original properties (Johnson and Lark-Horovitz 1949, Lark-Horovitz, Becker, Davis and Fan 1950). A fundamental difference thus exists between germanium and the other semiconductors. The silicon also showed new absorption bands which help interpretation in this case. These bands have been studied by Becker, Fan and Lark-Horovitz (1952), Fan (1952) and Fan and Becker (1951); the great decrease in longer wavelength absorption and the new band are both consistent with the introduction of both electron and hole traps.

The number of holes produced per incident neutron has been investigated by Crawford and Lark-Horovitz (1950 a, b). They found that n-type Ge loses electrons at an initial rate of 3 per incident fast neutron, while p-type Ge gains holes at a much slower rate, about 0·6 to 0·8 per incident neutron, although the past history and temperature affect this figure (Cleland, Crawford, Lark-Horovitz and Pigg 1951, Cleland, Crawford, Lark-Horovitz, Pigg and Young (1951 a).

Similar experiments with polonium alpha particles (Brattain and Pearson 1950) show that under this bombardment also, germanium changes from n- to p-type. The initial rate of electron loss is 78 per alpha particle, while after conversion, the initial rate of introduction of holes is 8·6 per alpha. Some of these holes disappear with time at room temperature after bombardment has ceased, leaving two per alpha particle. The initial high rate agrees well with the number of displaced atoms per 5 MEV alpha particle (59) calculated according to Seitz theory

If, however, the initial concentration of holes is high enough, then bombardment of p-type germanium will give a conductivity decrease (Crawford, Cleland, Lark-Horovitz, Pigg and Young 1952, Cleland, Crawford, Lark-Horovitz, Pigg and Young 1951 b). The hole concentration to which all specimens tend after a large bombardment, and which thus determines whether the conductivity increases or decreases, is itself a function of temperature. It is about $5 \times 10^{17}$ per $cm^3$ at 55°C and $4 \times 10^{16}$ per $cm^3$ at −78°C. Successive bombardments of a specimen with hole concentration between these values at the two temperatures give successive increases and decreases of conductivity. Similar effects with deuteron irradiation have also been reported (Forster, Fan and Lark-Horovitz 1952). The number of carriers lost per incident deuteron have also been determined for low resistivity n- and p-type germanium and p-type silicon. They are 11, 4 and 31 respectively.

A theory of this effect has been given by James and Lark-Horovitz (1951). If the interstitial caused by bombardment simply acted as a donor and the vacancy as an acceptor, then the bombardment would not change n-type germanium to p-type, for the same number of donors and acceptors would be formed and would largely annul each other's effect. The actual situation must be more complicated than a simple production of electron acceptors.

James and Lark-Horovitz suggest that the situation is best visualized by considering double ionization states of interstitials and vacancies. Consider an interstitial Ge atom with an electron removed from it : this electron will be attracted to the $Ge^+$ ion and will circulate round the ion in an orbit which will be large in diameter compared with the lattice spacing because of the dielectric constant of germanium. Its trapping energy will be about 0·05 ev. If we now consider the $Ge^+$ ion by itself, a further electron removed will have an orbit round the $Ge^{++}$ ion with an energy certainly four times that of the first electron's orbit and probably considerably higher, because its orbit would be too small for the simple calculation using the bulk dielectric constant to be valid. In fact, on the basis of the experimental results to be explained, this ionization energy is of the order of the width of the forbidden energy band. The energy levels are thus of the form shown in fig. 10 below.

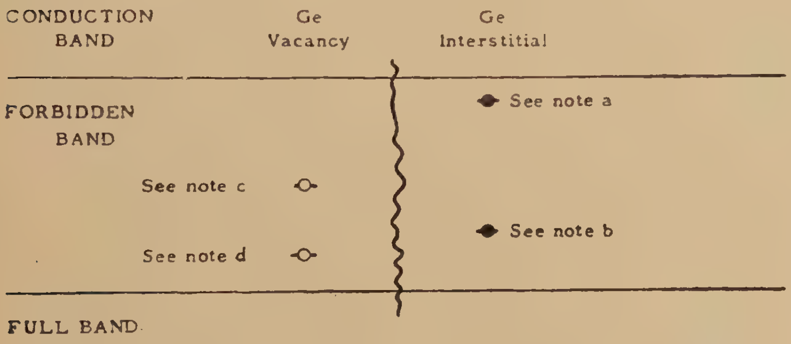
A similar argument can be used to discuss the levels caused by a vacancy. If a $Ge^{++++}$ ion is removed from the lattice, the band structure will be moved up at the vacant site and localized states will be formed above the full band. Let us suppose four states are split off and now, to restore neutrality, four electrons are removed ; the holes so caused will move to the excess charge and empty the four states above the band. To remove one of these holes, i.e. to force in an electron, energy is required, while a second hole will need more energy while third and fourth ones need not be considered. If only three states had been split off then, when the four electrons were removed, only three holes could go into these states and the remaining hole would circulate round the negative charge in a hydrogen-like orbit, and a state above 0·05 ev above the full band would be produced. If only two levels split off then two hydrogen-like orbits would exist and so on.

The difference between these various schemes is that the energy levels for the holes are different. Let us suppose that the levels are in some way like those shown in fig. 10, that is to say that the first two hole ionization levels and the second electron excitation level all lie near the bottom of the forbidden band.

Each vacancy interstitial pair provides two vacant levels that can trap two electrons from the conduction band, if (as in a n-type sample) there are any conduction electrons to be trapped. Thus for high conductivity germanium two electrons can be trapped per displaced atom, while for a lower initial number of electrons the number trapped will be somewhat less. The maximum resistance will be reached when bombardment has proceeded until all the conduction electrons are trapped in low lying levels and the top interstitial level is also empty. At this stage only one of the vacancy levels will be used to trap original conduction electrons, as the other will be needed to take electrons from the upper interstitial level. Thus the bombardment needed is twice as long as would be estimated from the initial slope. This prediction is in good agreement with experiment. Further bombardment will now give one empty vacancy level near the full band, and this can give the slow rise in p-type conductivity.

To explain the differing results in silicon one need only assume different dispositions of the levels, owing to the different dielectric constant. It appears that the final state of highly irradiated silicon leaves only levels which are far from being easily filled from the full band or excited to the conduction band. This can be directly related to a much greater second ionization energy for holes from silicon vacancies. In this state, the top two levels are always empty, the bottom two are always full.

Fig. 10

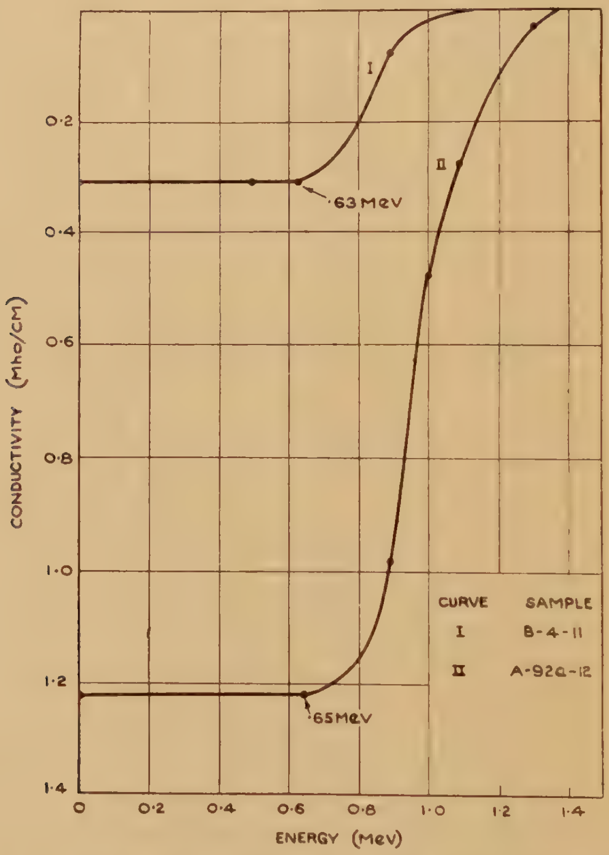


Level diagram for vacancies and interstitials in germanium.

(*a*) If occupied, the interstitial atom is neutral.
(*b*) If not occupied, the interstitial atom is doubly charged.
(*c*) If occupied, net charge of two electrons near vacancy.
(*d*) If not occupied, zero net charge near vacancy.

One of the most interesting experiments on semiconductors is the measurement of the energy needed to make a stable interstitial vacancy pair. This experiment has been performed by Klontz (1952, 1953 a, b ; see also Klontz and Lark-Horovitz 1951, 1952 a, b). A germanium sample cooled with liquid nitrogen, was bombarded in a Van de Graaff machine at various, well-defined energies. The conductivity change is found to have a threshold at about 0·6 MEV. If conductivity is plotted against energy of the bombarding particle, a curve is obtained (fig. 11) which rises with increasing energy, an initial upwards curvature before a linear range being due to the failure of the electrons in this region completely to penetrate the specimen. The actual value of the threshold, 0·65 MEV, would correspond to an electron which would, in a head-on collision with a stationary germanium atom, give 30 ev to the atom. This implies that 30 ev is the energy needed to displace an atom into an interstitial position known as the Wigner energy. Varley (private communication) has pointed out that if the thermal vibrations of the Ge atom are taken into account, the energy given over may be greater, and this effect might increase the figure obtained for the energy needed to form a stable interstitial–vacancy pair by about 2%. Other possible errors are introduced by the method of obtaining the threshold, especially as the cross section for displacement, as well as the volume of suitably irradiated material, is rapidly decreasing with energy. Nevertheless this represents a good quantitative measurement of the Wigner energy. Kohn (1954) has pointed out that some of the nearest interstitial sites can be reached with substantially smaller energies according to theory, and if this is true it implies that, either such sites are unstable at the temperature of Klontz's

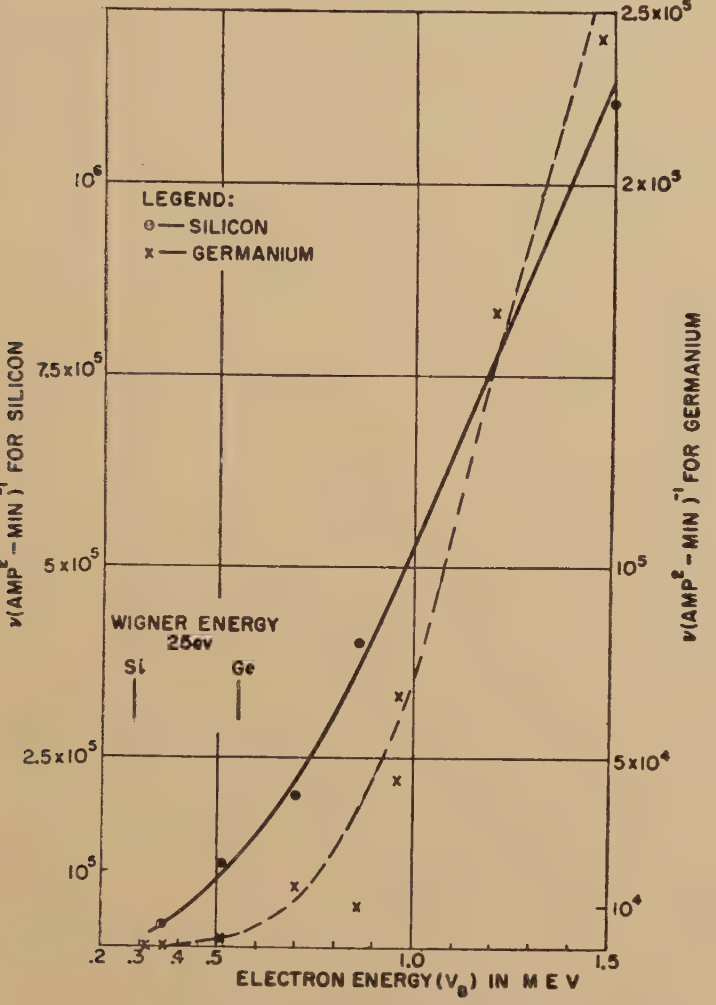
Fig. 11



Conductivity of two samples of germanium after bombardment with electrons as a function of the energy of the electrons (after Klontz 1952).

experiment, or that if stable they do not give the necessary acceptor levels. This, as Kohn suggests, is in agreement with the lower values of the Wigner energy found in other substances.

Fig. 12



The slope $\nu$ of the graph of $(I_s)^{-2}$ against time, which should be proportional to the number of defects present, against the energy of the bombarding electrons. (Loferski and Rappaport 1955.)

The minority carrier lifetime is a more sensitive measure of defects in semiconductors than the resistivity, and its use for threshold determinations was first suggested by Rappaport (1954 a, b). The use of this method has now been reported by Loferski and Rappaport (1955). They irradiated electron voltaic cells of germanium and silicon with electrons of energies varying between 0·5 and 1·3 Mev from a Van de Graaff machine, and measured the short circuit current. This was found to drop with time only if the electrons were above a certain critical voltage. In the theory of this effect $(I_s)^{-2}$ should be proportional to the number of defects produced, and thus plotting $(I_s)^{-2}$ against time should give a straight line whose slope $\nu$ is proportional to the rate of production of defects, and thus if $\nu$ is then plotted against the energy of the electrons, one should obtain a curve whose intercept with the energy axis gives the energy of an electron which can just displace an atom. The results obtained are shown in fig. 12, and it can be seen that an effect was observed in germanium (n-type of initial resistivity 0·2–0·4 ohm cm) at energies above 0·510 Mev, whereas in the silicon (p-type of initial resistivity 35 ohm cm) an effect was observed even at 0·3 Mev, and the extrapolated intercept is about 0·28 Mev. These values for the bombarding energy give displacement energies of 23 for germanium and 27·6 for silicon.* The value for germanium is considerably below Klontz's figure of 30 ev, so that the experiments are disagreeing by much more than their experimental errors. As Loferski and Rappaport's experiment was made at room temperature, the thermal vibrations of the atoms are more important, and the effect referred to when discussing Klontz's experiment might affect the answer by about 2·5 ev, but certainly not by enough to bring it up to Klontz's figure.

It is also perhaps a little unfortunate that Loferski and Rappaport used the same electrons to excite the cell and to cause the damage, as electrons below the energy to cause permanent damage might affect the minority carrier lifetime. However, if such damage is not permanent it should not increase indefinitely, and Loferski and Rappaport find that at 0·51 Mev the short circuit current showed a steady drop for 20 min.

As well as studying the threshold, Klontz has shown that electrons have the same effect as other particles on n- and p-type germanium; he has found the number of electron traps per incident electron at various energies (this varies from $10^{-3}$ electron traps per cm$^3$ per incident electron per cm$^2$ at 0·7 Mev to 1·1 at 1·5 Mev and 2·5 at 1·8 Mev) and he has also studied the annealing effects.

Klontz (1953 a, b) has also studied the effect of electron bombardment on a highly conducting sample of p-type germanium. As with neutrons, bombardment at liquid nitrogen temperature decreases the conductivity, presumably tending towards the same limiting value as is approached by an increase of p-type conductivity in low conductivity or n-type samples. Room temperature anneals were sufficient to cause almost complete recovery and some changes were observed even at liquid nitrogen temperature.

Cussins (1955) has studied the effects on germanium of bombardment with ions from $^1$H to $^{51}$Sb at about 5 kev. The effects he observes in the diode characteristics are consistent with the production of a p-type layer on the surface. Cussins considers that his results are not, however, consistent with the simple Lark-Horovitz theory, as they require two types of acceptor defects, and as saturation occurs at a concentration of only 1 : $10^6$. Further the penetration does not seem to depend on the nature of the ion. Cussins explains his results in terms of a thermal spike picture. Similar experiments are reported by Lawrance, Gibson and Granville (1954).

---

* *Note added in proof.*—Rappaport and Loferski (private communication) have since found measurable effects at lower energies, and their value for $E_d$ is now 12·9 ev in both germanium and silicon.

The comparatively straightforward explanation of all the effects in terms of the energy levels associated with vacancies and interstitials is complicated by the effects observed when germanium is bombarded at liquid nitrogen temperature and subsequently warmed. Under these circumstances Forster, Fan and Lark-Horovitz (1953), Fan and Lark-Horovitz (1955) found that bombardment with 9·3 MeV deuterons converted n-type to p-type and reduced the conductivity of high conductivity p-type just as at room temperature, but that the effect of raising the temperature was unusual. For temperatures below 141°K both resistivity and Hall coefficient increased, while above this temperature they decreased again until at room temperature they were both about six orders of magnitude lower than at the end of the irradiation when measured at the same temperature (90°K). Thus annealing had made the originally n-type sample much more p-type than the irradiation had, so much so that a p-type sample of the same resistivity as that finally achieved would have increased its resistivity if bombarded at 90°K. All this implies that a large number of donor impurities have annealed out below room temperature, a result confirmed by mobility measurements. Similar experiments with electron bombardment gave quite different results. Annealing at 90°K or 130°K after the irradiation made the Hall coefficient and resistivity drop, but further annealing at 170°K restored both to values very close to those they had at the end of bombardment. Further annealing at higher temperatures in the case tended to restore the properties before irradiation. Other experiments of this type, in which resistivity and Hall coefficient are measured during low temperature bombardment and annealing, have been reported by Klontz (1953 a, b), Pepper, Klontz, Lark-Horovitz and MacKay (1954), Klontz, Pepper and Lark-Horovitz (1955) and Stoeckman, Klontz, Fan and Lark-Horovitz (1955); also by Brown, Fletcher and Wright (1954) and Shulman, Brown and Fletcher (1954). The results of experiments on neutron irradiation at 110°K have been reported by Crawford, Cleland, Holmes and Pigg (1953), Cleland, Crawford and Pigg (1955). The fact that various annealing processes occur below room temperature, and also that electron and heavy particle bombardment produces different results, shows that the simple picture of damage in terms of vacancy and interstitial levels must be amplified. The general ideas in this model may well remain, but the number of defects considered must be increased, possibly to include clusters.

With the techniques available it is possible to find the positions of the various levels introduced, and further work will have to be devoted to a painstaking study of these positions, and their correlation with the behaviour of defects. The way in which this work is being done, and some preliminary results, are reported by Fan and Lark-Horovitz (1955).

The various effects in silicon and germanium have been compared with similar effects produced by quenching (which should produce vacancies, and possibly also interstitials as the structures are very open). Taylor (1952) has found that only hole traps are observed in quenched germanium, while both electron and hole traps are found in silicon. The number as a function of quenching temperature allowed a calculation of the formation energy, which was found to be $1\cdot8-(5\times10^{-4}T)$ ev per atom in germanium. Mayburg has found similar results in germanium, and has studied the annealing, which he interprets in terms of vacancies and interstitials in much the same way as is done in the radiation damage experiments. Below 516°c he finds that the best model for the annealing is one in which interstitials are trapped at dislocations. He therefore suspects that interstitials are more mobile than vacancies in germanium.

Ellis and Greiner (1953) have studied the properties of plastically deformed germanium, and in this case, as with irradiation, heavily damaged n-type specimens are found to be converted to p-type. The results are not, however, completely similar to those obtained by irradiation, as Lipson, Burstein and Smith (1955) find that the intrinsic absorption edge is shifted in cold-worked germanium, but not in irradiated, and the tail of the absorption edge has a different character in the two cases.

Other effects which should be mentioned here are that Taylor, Odell and Fan (1952) have found that the high non-ohmic resistance of grain boundaries in n-type germanium is eliminated if the material is converted to p-type by irradiation or heat treatment, and that Florida, Holt and Stephen (1954) have found that neutron irradiation reduces the hole storage effects (presumably by reducing hole lifetime) in point type transistors.

The annealing of bombardment damage in germanium above room temperature has been studied by Brown and Fletcher (1953), Fletcher, Brown and Machlup (1953), Brown, Fletcher and Machlup (1953), Brown, Fletcher and Wright (1953), Fletcher and Brown (1953). Samples of germanium, initially n-type with conductivity of about 1 mho cm were bombarded with 3 mev electrons at room temperature and then annealed at various temperatures from 140° to 360°c. The annealing curves at different temperatures could be made to overlap by a suitable adjustment of the time scales, although the form of the recovery curve at any one temperature is not that of a simple rate process. From the factors needed to bring the curves at different temperatures into coincidence, an activation energy of 1·7 ev was deduced, although the points were better fitted by a curve, implying that the initial stages of recovery required a lower activation energy of about 1·6 ev. The theory of this recovery has been discussed by Fletcher and Brown (1953). They consider that the annealing is the sum of three terms. One is a monomolecular term due to the recombination of vacancy–interstitial pairs close to one another; this process will have an activation energy depending on the initial separation and can thus be represented as the sum of a series of terms for all the possible positions, a sum that can be calculated—as has already been mentioned for the case of face centred cubic metals—and which Fletcher and Brown have done for the germanium lattice. The number of vacancy–interstitial pairs annealed in this way will be

$$N_M = \Sigma_1 N_i \exp(-t/\tau_1)$$

where $N_i$ is the number of interstitials at the $i$th site from their vacancy, $\tau_1$ is the jump time for the first move (which will be the longest part of the whole recombination process) and $\Sigma_1$ the sum over all sites within a certain radius.

A second process will occur when the vacancy and interstitial are not close enough together to be in each other's stress field. In the course of diffusing about, the mobile partner (assumed by Fletcher and Brown to be the vacancy) may wander sufficiently close to the other to be attracted by this stress field and be annihilated, or it may escape. The number which are annihilated in this way will, on a continuum theory, be given by a term of the form

$$N_L = \Sigma_2 N_i \frac{r_c}{r_i} \operatorname{erf}\left[\frac{r_i - r_c}{(2\langle b^2\rangle)^{1/2}} \left\{\frac{\tau}{t}\right\}^{1/2}\right],$$

where $r_i$ is the distance of $i$th site from its vacancy, $b$ the magnitude of the change in $r_i$ for each jump, $\langle\ \rangle$ means the average over all possible jumps and $\Sigma_2$ is the sum over all sites outside the radius $r_c$.

Finally we have to consider the number of sites lost by bimolecular recombination of interstitials with vacancies other than those originally nearest to them. This gives another term for the loss of the number of pairs or, perhaps, there may be other terms depending on capture at surfaces or dislocations.

$$N_B = \Sigma_2 N_i \left(1 - \frac{r_c}{r_i}\right) \Big/ \left[1 + 4\pi r_c^2 \langle b\rangle \left\{\frac{t}{\tau}\right\} \Sigma_2 N_i \left(1 - \frac{r_c}{r_i}\right)\right].$$

The total loss of pairs of vacancies and interstitials is therefore

$$N = N_M + N_L + N_B.$$

After a certain time $N_M$ will become negligible, since $\tau_1 < \tau$, and the second mechanism requires many jumps of time $\tau$, while the monomolecular mechanism essentially requires one of time $\tau_1$.

In comparing a theory of this degree of complexity with experiment, a large number of possibilities emerge. A successful theory must not only reproduce the annealing curve, since with so many parameters it could hardly fail to do this, but it must also show that plausible values of the constants are used, such as jump time $\tau$ and the radius of the elastic field round an interstitial $r_c$.

Brown, Fletcher and Wright (1953) consider various probabilities, and eventually decide that only the first two terms enter appreciably in their experiments, and that the first, monomolecular, term has two components. As the radius $r_c$ comes out to be such that about three ' shells ' of neighbouring atoms surround an interstitial they suggest that the nearest possible locations for the vacancy are unstable—at least at room temperature.

They discount the possibility of fitting with just the second and third terms, and assuming that the first process all occurs below room temperature, because of the variation of activation energy with temperature (the second and third terms would require a constant energy) and because the jump time deduced in this case is $10^{17}$/sec, compared with an expected value of $\sim 10^{13}$, which is in agreement on the other method of fitting. Another difficulty in fitting in this way is that the fact that 10% of the change remains after both processes are complete has now to be associated with diffusion to surfaces or dislocations, and even this can only explain it if the interstitial moves or alternatively is the acceptor rather than the donor, neither of which they regard as acceptable.

In view of results on copper–gold, which point strongly to interstitials as being more mobile in that case, it may seem surprising that in germanium vacancies are assumed to be the mobile element, but it must be remembered that germanium is very far from being close packed, having the diamond lattice, and that interstitials are therefore very different in this than in a close packed lattice. A set of natural interstitial sites exist, in which it may be imagined that the atom can remain with little elastic distortion of the lattice, whereas no such sites exist in the close packed case. While this does not prove that the activation energy for diffusion of interstitials is as high or higher than that for the diffusion of vacancies, it at least shows that this is not ruled out by analogy with the close packed metals. The results of Mayburg (1954) do however suggest that in germanium interstitials may still be the more mobile defects.

Another result reported by Fletcher, Brown and Wright (1954) is that the rate of change of conductivity changes as electron bombardment proceeds. This cannot be due to an approach to the Fermi level, and they have performed further experiments to see whether it can be attributed to bombardment annealing. If this were the cause, it might be expected that bombardment at 1·5 MeV might anneal damage caused by a previous bombardment at 3 MeV and also that a saturation state would be reached on prolonged bombardment at any one energy. Neither of these effects was observed, and so Fletcher, Brown and Wright deduce that the effect must be due to a microscopically non-uniform distribution of impurities.

On other semiconductors the effect of bombardment is to reduce the conductivity. Pigg, Cleland, Crawford and Lark-Horovitz (1951) found that copper oxide plates decreased in conductivity on pile irradiation, initially quite rapidly, as did the forward conductance of $Cu_2O$ rectifiers ; the reverse conductance dropped only slightly. The effects in silicon have already been discussed above, both n- and p-type show a decrease in conductivity. The effect of bombardment by polonium alpha particles on lead sulphide semiconductors has been studied by Odencrantz (1952). He found that the conductivity initially increased several per cent and then decreased to one-third of its initial value, recovery requiring several days.

Cleland and Crawford (1954 a, b, c) have reported that another semiconductor which changes its type on neutron irradiation is indium antimonide. In this case holes are removed from p-type material four times as fast as electrons from low resistivity n-type samples, and both types tend towards n-type with a carrier concentration of about $10^5$ electrons/cm$^3$ at liquid nitrogen temperature. The variation of Hall coefficient and resistivity have been followed during electron bombardment by Pepper, Klontz, Lark-Horovitz and MacKay (1954) ; the two vary similarly for p-type, while for n-type the Hall coefficient passes through a maximum negative value and then becomes positive. The effects here must be expected to be more complicated than the corresponding effects in germanium, as there are now two possible sorts of interstitials, and two sorts of vacancies. Until the germanium data are explained, it is probably impossible to give a theory of the more complex semiconductors. Another that has been investigated is gallium antimonide. Here Cleland and Crawford (1955) found that neutron irradiation reduced the carrier concentration in high conductivity samples of both p- and n-type, the rate of reduction being about the same for both, and no changes of type were observed. Some annealing of the damage occurred at 120°c, but at 500°c the number of acceptor centres in p-type increased markedly, while in n-type the number of donors markedly decreased ; irradiation of the resulting low conductivity n-type samples (such a value is not obtainable in other ways), showed that in n-type samples the rate of carrier removal is not very dependent on initial carrier concentration, while for p-type samples, the rate of carrier removal dropped rapidly with lower initial concentration. This presumably indicates that, if the effect did not saturate before, n-type gallium antimonide would be converted to p-type.

A rather special case, intermediate between a metal and a semiconductor, is graphite, where the conduction and valence bands touch or just overlap. Kinchin (1954) has summarized the effects which are observed on irradiation in this case. The resistivity increases, the increase being greater if it is measured at a higher temperature ; the Hall coefficient, initially negative, increases through zero with bombardment. When measured at low temperatures the Hall coefficient shows a maximum at a given irradiation, after which further irradiation decreases it again. These data have been used by Johnston (1955) to calculate the density of defects. After $5 \times 10^{19}$ nvt of thermal neutrons, the density of electron trapping defects is $10^{20}$ per $cm^3$.

### 12.2. *Other Effects in Semiconductors*

The variations in the number of carriers in germanium can be expected to affect the diamagnetism. Stevens, Cleland and Crawford (1954) and Stevens (1954) have reported measurements on both n- and p-type samples. In the p-type sample the effect of irradiation was to decrease the diamagnetic susceptibility at low temperatures, in agreement with predictions from the electrical effects, but no change was observed in the n-type sample, a fact which Stevens attributes to an insufficient initial carrier concentration and also to possible inhomogeneities.

Schulz-DuBois, Nisenoff, Fan and Lark-Horovitz (1955) have found electron spin resonance in p-type, boron doped silicon after neutron irradiation, though no such effect could be found before irradiation, and this is therefore a method of investigation which may give useful additional data for the interpretation of the various effects occurring.

The x-ray and electron diffraction patterns of irradiated germanium and silicon have been studied by Binnie and Liebschutz (1952, 1953 a, b, 1954). They have directed attention to the diffuse x-ray scattering, as this should be sensitive to local lattice disturbances, and should also allow a calculation of the elastic constants by Wooster's method ; they have also studied the Kikuchi lines in electron diffraction, as these are also highly sensitive to the regularity of the lattice. Specimens of germanium cyclotron irradiation at $-5^{\circ}$c were used in the x-ray studies, and specimens irradiated at liquid nitrogen temperature and also in a reactor in the electron diffraction experiment. No changes in any of the patterns were observed, and no change in the lattice parameters of neutron bombarded germanium were found. In silicon, however, Binnie and Liebschutz (1954) found definite changes in the diffuse x-ray scattering, which corresponded to large changes in the elastic constants, particularly $C_{11}$ and $C_{12}$. The value of the change in Debye temperature calculated from these values was in agreement with the change observed. Weissman and Chang (1955) have reported a 0·02% change in the *a* lattice parameter of a germanium single crystal, and also an increase by more than a factor three in the width of the (111) reflexion after reactor irradiation.

Keesom, Lark-Horovitz and Pearlman (1952 a, b, 1953) have found that the linear electronic contribution to the specific heat of silicon at very low temperatures is much reduced by bombardment either with deuterons or neutrons, thus confirming that the number of carriers is reduced. They also found that the Debye temperature is reduced (as measured electrically), and in order to account for the magnitude of the change observed, Dienes and Kleinman (1953) suggest that some other form of damage than vacancies and interstitials must be called upon. They suggest that in structures such as silicon and diamond some covalent single bonds are broken, and reform as double bonds. Calculations show that each fast neutron gives a region 45 Å in diameter in which many bonds are broken, leading to a weakened structure with a great reduction in the elastic constants. Such a process has no analogue in true metals : other effects of bombardment on covalent and ionic materials will be discussed in § 13 below.

The lattice of graphite also shows changes on irradiation. The *c* lattice spacing increases on bombardment, at room temperature by 1·3% for an irradiation of $10^{20}$ nvt (Simmonds, private communication) and by 4·75% for an irradiation of $10^{20}$ nvt at −196°c (Keating 1955 b). At the lower temperature the expansion is not proportional to dose. The x-ray reflections also broaden considerably, and give long ‘ tails ’.

## § 13. ANALOGOUS RADIATION EFFECTS IN NON-METALS

### 13.1. *Introduction*

A review of radiation damage effects, even one primarily concerned with effects in metals, would be incomplete if it contained no reference to analogous effects in non-metals. The type of process which we have envisaged as responsible for the observed change in metals can operate equally well in any solid, and, while other effects are to be anticipated in materials in which displaced electrons can also give lasting effects, it might be expected that effects due to displaced atoms could be differentiated from the purely electronic effects both theoretically and also empirically, as heavy particles should alone be capable of displacing atoms from their lattice sites. Unfortunately this expectation does not prove to be well founded. Not only are the effects of x-irradiation and heavy particle irradiation similar, but some of the effects produced by x-rays in ionic solids seem to be explicable only in terms of atoms displaced by the radiation. The process by which this occurs is probably electronic in origin, and does not seem to occur in metals, though as materials of intermediate character are studied, it should always be remembered as a possibility.

Two mechanisms whereby x-rays could produce displaced atoms in ionic solids have so far been suggested ; the first (Markham 1952, Pratt 1955) is that vacancies are removed from dislocations, possibly by the action of excitons ; the other (Varley 1954 a, b) is that multiple ionization by the radiation may force an originally negative ion to leave its position under the action of electrostatic forces from its positively charged neighbours, thus creating a vacancy–interstitial pair.

Because of the existence of these effects, much care must be exercised in comparing the results obtained on non-metals with those in metals, and in this section we shall simply mention some of the effects which seem at present to be most nearly analogous to effects in metals, or which are most illustrative of the underlying processes, without claiming to review in detail this very large and complex subject.

### 13.2. *Mechanical Properties*

In ionic crystals quite large changes in the plastic properties have been reported. Vaughan, Leivo and Smoluchowski (1953), Smoluchowski, Leivo, Pearlstein, Smith and Vaughan (1953) found that proton irradiation raised the hardness of NaCl, measured in a Tukon tester, from 16·3 to 36. Westervelt (1953, 1954) has confirmed this result, and has also reported similar increases on electron and x-irradiation ; in fact increases of over 100% were obtained with all these bombardments, the effects annealing between 150° and 350°c. An even greater increase (to 46 VPN compared with 36 VPN with electrons and 33·4 VPN with x-rays for NaCl whose original hardness was 16·3) was obtained with alpha particles. That these effects can be produced by radiation which is incapable of dislodging an atom by a direct collision shows that some mechanism such as those discussed in the last paragraph must be acting.

Further effects that have been reported in ionic crystals are that irradiation reduces the internal friction (Frankl and Read 1953, Frankl 1953) and increases the yield stress, though after an initial decrease at low fluxes (Pratt 1955). Pratt interprets his initial decrease to the freeing of jogs from dislocations, and the subsequent increase to the creation of further jogs.

The Young's modulus of ionic crystals is also increased by proton irradiation according to Vaughan, Leivo and Smoluchowski (1953), although Gordon and Nowick (1955) report that x-irradiation raises the modulus $C_{11}$ only of cold-worked rock salt. In their case the irradiation effectively removed the decrease of modulus caused by the cold work. There may be here a genuine difference between the effects of the different radiations.

### 13.3. *X-ray, Electron and Neutron Diffraction and Density*

In ionic solids a series of experiments has been performed on the effects of irradiation on the lattice parameters as determined from the x-ray diffraction and on the density. Such experiments taken together should be able to distinguish between damaged states in which vacancies predominate and those in which vacancies and interstitials are present in roughly equal numbers. Unfortunately the reported measurements do not agree. Binder and Sturm (1954 a, b) and Keating (1955 a) have both studied the effects of reactor irradiation on lithium fluoride. As lithium breaks up under neutron bombardment to give a triton and an alpha particle with 4·8 MEV between them, the damage that can be produced is intense. Binder and Sturm find that the changes of x-ray density and macroscopic density are equivalent to within 6%, so that the damage would not appear to be primarily vacancies, but Keating found no change in lattice parameter after $7{\cdot}5\times10^{17}$ nvt, although a broadening of the lines and a reduction of the extinction occurred, and this throws doubt on the results. Warren (1951, 1952, 1953, 1954) also found that broadening of the peaks was the main effect in LiF, and he attributed this to a greater range of spacings occurring within the crystal. The integrated intensity of the (002) peak also increased, but not that of the (004) or higher order peaks. On the other hand Berry (1955) found that X-irradiation gave an increase in the lattice dimensions of potassium chloride, which saturated at $1\times10^{-5}$, as compared with changes of length of $\sim20\times10^{-5}$ reported by other workers. Berry interprets his result in terms of the production of vacancies, though calculations would be needed to see whether the observed lattice expansion could be caused by vacancies, or whether it is evidence for the production of a small number of interstitials by the X-rays.

Further evidence of the change of volume of LiF has been obtained by Primak, Delbecq and Yuster (1955), Primak, Yuster and Delbecq (1955). They found that non-uniformly irradiated crystals were birefringent, and interpreted this birefringence as a photoelastic effect due to the change of volume of the irradiated parts. After an irradiation of $10^{13}$ deuterons per cm$^2$ the volume change calculated from the birefringence was 2 to $9\times10^{-5}$, depending on the depth. As the number of vacancies could also be determined from the density of the coloration, it was possible to compare the dilatation with the density of vacancies, and it was found that the two agreed to within the error of the experiment.

In potassium chloride Leivo (1953) has found a density decrease of $5\times10^{-5}$ g cm$^{-3}$ by measuring the suspension temperature in 1–3 dibromopropane before and after one hour's irradiation with 360 MEV protons; and has also obtained similar effects with X-rays. An effect four times as large has been reported by Leivo and Smoluchowski (1954) after longer irradiation. A study of the surface of these crystals by Smith, Leivo and Smoluchowski (1954) using interferometric methods, gave no evidence that diffusion was responsible for these density changes, but they report that slip lines were often visible in the irradiated areas.

In potassium and sodium chloride, Lin and Russell (1955) have measured the change of length of crystals on X-irradiation, and compared this with the F-centre density determined optically. Agreement to within 5% was obtained; thus in KCl, when the change of length per unit length was $1{\cdot}36\times10^{-6}$, the number of vacancies calculated from this is $6{\cdot}6\times10^{16}$ cm$^{-3}$, whereas the number determined optically was $6{\cdot}7\times10^{16}$ cm$^{-3}$. This again shows the X-irradiation produces vacancies, if not interstitials, in ionic crystals.

In covalent compounds the effects can be even more spectacular, and in some cases the crystal lattice can be completely broken down by bombardment and reduced to a glass-like state. This effect has long been known to mineralogists, for some minerals which have radioactive atoms either as constituents or impurities have reached this state in which the external appearance of the mineral shows that it has been crystalline in the past, although it shows no anisotropy, cleavage, or crystalline x-ray pattern. This state is called the metamict state. The most surprising fact is that some substances become metamict while others do not. The problem has been considered from the evidence obtained with pile neutron bombardment by Primak (1954, see also Primak, Fuchs and Day 1953). He found that reactor irradiation produced no effect on the powder patterns of beryl, $GeO_2$, germanium, silicon, corundum or rutile; produced small increases in the lattice constants of MgO (0·1%), spinel (0·12%), and $CaF_2$ (0·08%): and produced large changes but no diffuseness in diamond (0·9%), silicon carbide (0·68% in $a_0$, 0·68% in $c_0$), chrysoberyl, and phenacite: and diffuseness in quartz, trydimite and cristobalite. He came to the conclusion that large effects were not associated with crystal structure or bond type, but only with the existence of a quasi-stable vitreous state.

The extreme lengths to which this process can go are well illustrated by the behaviour of the mineral zircon (Hurley and Fairburn 1952, 1953, Holland and Gottfried 1955), as this mineral can contain various amounts of uranium and thorium as impurities, and so gives samples which have had various doses up to $10^{16}$ alpha particles per milligram. The intensity of the x-ray diffraction peaks decreases with dose, and becomes immeasurable above background at about $6 \times 10^{15}$ $\alpha$/mg. Simultaneously the diffraction peaks shift, and at an intermediate stage a second peak appears, attributed by Holland and Gottfried to a second phase. Later, this peak too disappears into the background. All these data, especially when it is realized that the radiation has occurred over about a thousand million years, imply that the annealing rate is quite negligible at ambient temperatures, although metamict minerals almost always recrystallize when heated, though not necessarily to the lattice from which they originated.

An interesting case of metamictization which has been produced in reactors, but which never occurs in nature is quartz. As quartz is sometimes found close to radioactive deposits, this may imply that slow annealing can occur at ambient temperatures, though not fast enough to have any effect on the laboratory experiments. Wittels (1953) has observed that on irradiation quartz becomes at first more anisotropic, the Debye–Scherrer rings are smeared out and the symmetry of the Laue patterns disappears. At this stage the density change was 4·8% as determined from the x-ray pattern, and 3·5% determined mechanically. Further irradiation (Wittels and Sherrill 1954) decreased the density still further, by 14·7% in all, and made the x-ray lines disappear: the crystals no longer gave a latent heat at the $\alpha \rightleftharpoons \beta$ inversion, and piezoelectric crystals no longer resonated. What is more, samples which were originally quartz, low cristobalite, low tridymite and quartz glass were all reduced to a common phase, a glass which was optically isotropic and had a specific gravity of 2·26. In all cases this glass recrystallized by annealing at 930°C to quartz. The early stages of this damage have also been studied by Johnson and Pease (1954), who found that a quartz crystal oscillator at first suffered a rather rapid reduction of frequency, due to ionization, but also showed a slow linear decrease attributed to the creation of defects by the neutrons ; after neutron irradiation the quartz became transparent, and could no longer be coloured nor have its frequency changed by x-rays. One of the features of irradiation damage in quartz noticed by Wittels and Sherrill (1954) was that the density change accelerated as the irradiation proceeded up to about $10^{20}$ nvt. Primak (1955) has suggested that this is due to thermal spikes having a greater effect when the thermal conductivity of the quartz has been reduced by earlier damage. It is however possible that this phenomenon may be due to the inception of a new form of damage, such as the breakdown of the lattice.

The compounds of boron have also been studied in some detail, as the $^{10}B(n, \alpha)$ reaction gives large effects in pile irradiation. Pease (1954) has studied a series of boron compounds and obtained lattice parameter changes of the order of 1% at doses of about $10^{18}$ thermal neutrons per $cm^2$. A marked saturation effect was found to occur fairly early in the increase of the $c$ spacing and decrease of the $a$ spacing, although other effects, such as the broadening of some x-ray lines, did not saturate ; this is presumably due to a limitation on the number of interstitials that can exist, while other forms of damage, such as misorientations, can continue to build up. Tucker and Senio (1954 a, b, 1955 a, b) have studied boron carbide in some detail at heavy irradiations, and obtained very marked effects. They found a contraction in the $c$ direction and an expansion in the $a$ direction, changes in the average position of certain atoms and very heavy diffuse scattering. In diamond, also, the scattering angle increases by 10′ to 30′ on proton irradiation (Hayes and Smoluchowski 1953) and a new maximum appears in the x-ray pattern (Robinson, Li and Smoluchowski 1954).

Antal, Weiss and Dienes (1955) have suggested the use of long wavelength neutron transmission to determine the number of defects in irradiated solids, and report that preliminary results on $Al_2O_3$ are promising. If the wavelength of the neutrons is long in comparison with any Bragg scattering wavelength, then only defects can cause scattering out of the beam, and this will be the only attenuation if the nuclei concerned do not capture neutrons. Further, the scattering of a defect will be simply that of the nucleus concerned, and can be known accurately from nuclear experiments. Therefore the method in principle allows a direct measurement of the number of defects. In practice the method may be somewhat limited in scope. The restriction to materials with low capture cross sections does not allow very many materials to be investigated, and the specimen will probably have to be very large (or the order of a metre long) to obtain an accurately measurable attentuation. Further, it is not obvious what the effect of clustering of defects will be.

Another material that shows a probable change of phase besides those mentioned in § 9 is phosphorus. Chipman, Warren and Dienes

(1953) have found that irradiation increased the *c* spacing of black phosphorus by 0·03±0·02%, and also that other lines appeared in the diffraction pattern, some of which could be identified as some of the lines of red phosphorus. In addition to the X-ray changes, the sample became stronger and harder and showed less tendency to absorb water.

### 13.4. *Diffusion and Electrical Conductivity*

In ionic substances the electrical conductivity is believed to occur by the diffusion of positive ion vacancies, so that irradiation should affect both the conductivity and the diffusion in much the same way. X-irradiation decreases the diffusion coefficient of sodium ions in NaCl (Mapother 1953), and also reduces the electrical conductivity of KCl (Nelson, Sproull and Caswell 1953). This is also in agreement with the observation reported above that X-irradiation reduces the internal friction. However, Nelson *et al.* found that further irradiation led to an increase in conductivity again, a result they found also with neutrons.

Pearlstein (1953 a, b, 1954, see also Smoluchowski 1955) has studied in detail the effect of bombarding NaCl and KCl with 400 MEV protons and with gamma rays. He confirmed that for small bombardments the conductivity dropped, while for larger ones it increased again, and further found that the annealing characteristics were complex. At first on annealing the conductivity rapidly decreased to under 1/100 of the conductivity of an unirradiated control, and then on further heating the conductivity rose again, with suggestions of further oscillations, to its unirradiated value. Smoluchowski (1954, 1955) has discussed these results in terms of the production, clustering, and loss of vacancies and interstitials, but which are involved at which stages is far from settled.

### 13.5. *Thermal Conductivity*

The effect of neutron irradiation on the low temperature thermal conductivity of quartz has been investigated by Berman, Klemens, Simon and Fry (1950), Berman (1951), Klemens (1951). Irradiation reduced the thermal conductivity of quartz, particularly in the region of the conductivity maximum at about 12°K, and with sufficiently large doses, suppressed the maximum. At this stage the curve of conductivity versus temperature was more like that of a quartz glass (in agreement with the observations of Wittels and Sherrill (1954)). Annealing gradually restored the original properties. The results have been analysed by Klemens (1951) in terms of the scattering caused by clusters of defects, which will affect the low frequency phonons at low temperatures, and assuming a reasonable size for the clusters, Klemens deduced a density of $10^{-7}$ clusters per atom. The concept of clustered defects seemed adequate to explain the data.

Similar experiments on synthetic sapphire crystals have been reported by Berman, Foster and Rosenberg (1955), with somewhat similar results. In this case the result can be interpreted as showing that one neutron affects a region containing 4000 atoms in a long, thin volume. Gamma radiation had a rather similar effect, but the damage appeared to saturate before the full reduction obtainable with neutrons was reached. In diamond gamma irradiation gave no effect, though neutron irradiation did.

### 13.6. *Magnetic Susceptibility*

If interstitials or vacancies have an intrinsic magnetic moment, then irradiation should make a material more paramagnetic, and in line with this, a reduction of diamagnetic susceptibility on irradiation has been observed by McClelland (1953) and McClelland and Donoghue (1953) in quartz and fused silica, recrystallized alumina and MgO, though no change was observed in sapphire, spinel and BeO. If the paramagnetism is due to the production of defects of spin $\frac{1}{2}$, their number can be estimated. After $3{\cdot}76 \times 10^{19}$ nvt the numbers obtained are $2{\cdot}1 \times 10^{-3}$ per molecule in silica glass, $3{\cdot}2 \times 10^{-3}$ in crystalline silica, $2{\cdot}4 \times 10^{-3}$ in recrystallized alumina, and $0{\cdot}65 \times 10^{-3}$ in MgO. In the first three some saturation of the effect was observed, but in MgO, in two separate tests, the effect of $0{\cdot}52 \times 10^{19}$ nvt was quite small, whereas $3{\cdot}76 \times 10^{19}$ nvt produced an effect eight times larger, which shows that, in this case at least, the effect is more complex than the simple production of a paramagnetic defect. Stevens (1955) has measured the temperature dependence of the susceptibility of quartz crystals. Before irradiation the diamagnetic susceptibility was largely temperature independent, whereas after irradiation the susceptibility decreased markedly if the temperature was raised. This confirms that paramagnetic centres have been introduced. After a certain irradiation the number of apparent centres decreased on further irradiation, although the density continued to decrease ; presumably this is because the damage at first is in the form of paramagnetic defects such as interstitial atoms, but that further irradiation brings the quartz nearer to the glassy state, and that after a certain time, the number of interstitials actually decreases.

The effect on the absorption of electromagnetic radiation has been suggested as a useful method for the study of irradiation damage by Duhamel, Freymann and Freymann (1953). They measured the effect of neutron irradiation on the absorption in the 0·2–1000 kc/sec range in ZnO, and found an appreciable effect ; by correlation of the frequency of maximum absorption with temperature, activation energies can be obtained.

Paramagnetic resonance methods can also be used to study the nature of the defects ; Griffiths, Owen and Ward (1954, 1955) have studied the effects in diamond and quartz ; the theory of the method has been discussed by O'Brien and Pryce (1955). In quartz it has been possible to show that the defect responsible for the ‘ smoky ’ coloration is in fact an aluminium impurity.

### 13.7. *Optical Effects*

In general the optical effects produced by irradiation are similar to those produced by other methods of coloration, but sometimes bands appear that do not seem to be produced in other ways. However, interpretation of these phenomena is still at an early stage, and the general effects do not seem to be analogous to those in metals, and so will be pursued no further here.

## § 14. SUMMARY

In this section an attempt will be made to collect the various data already reviewed to form a picture of the processes occurring in radiation damage.

### 14.1. *Nature of Damage*

The damage produced by irradiation of solids, other than chemical. electronic and transmutation effects, can best be described in terms of the creation of vacancies and interstitials. Except in the case of electron bombardment, these imperfections are not distributed evenly, but are concentrated in small volumes in the material. Provided the temperature is sufficiently low, and the original material in a stable state, no other effects are observed. If the material is not in a stable state, the transient existence of vacancy–interstitial pairs which are totally unstable, may give rise to nuclei of the more stable phase.

When heavy bombarding particles are used, local effects can be produced which are best described in terms of locally raising a small volume to a high temperature and quenching it. This has been demonstrated in the disordering of ordered alloys and more convincingly, in the production of regions of an unstable phase in a 2·4% Fe in Cu alloy by Denney (1954 b), although this result can also be interpreted in terms of replacement collisions (Kinchin and Pease 1955 a, b).

### 14.2. *Energy Needed to Produce the Damage*

In order to find the energy needed to produce the damage, it is necessary to use a particle whose energy is conveniently regulated near this threshold. It has been found that electrons are most convenient for this purpose, and several experiments have been performed in which electrons of varying energy have been used to produce bombardment effects. The highest energy at which no effect is produced is taken to be that energy with which an electron, in a head-on collision with a nucleus, just fails to impart enough energy to displace this atom to a distance at which it is in a stable interstitial site. The distance between a vacancy and an interstitial in the closest stable site is not known, and may be a function of temperature, but nevertheless these experiments give a measure of the energy required to form vacancy–interstitial pairs. As they are of such fundamental interest in the study of radiation damage, these experiments are listed in table 3.

In this table the last column shows the energy which an electron of the energy shown in the preceding column would give to an atom in a head-on collision. The accuracy in each is of the order of a few per cent.

There is, as yet, no accurate theoretical figure with which to compare these results. Huntington (1954) has reported that an attempt is being made to remedy this, but at present the best theory gives a value of 34 ev for the minimum energy necessary to produce a vacancy–interstitial pair in copper, the assumptions being made such that the 25 ev found by Eggen and Laubenstein falls well within the possible limits.

Table 3. Experiments to find the Energy needed to form a Vacancy–Interstitial Pair

| Author | Bombarded material | Property measured | Energy threshold (MEV) | Energy given to an atom (ev) |
|---|---|---|---|---|
| Klontz (1952) | n-germanium at −196°C | resistivity | 0·63 | 30 |
| Loferski and Rappaport (1955) | n-germanium and p-silicon at room $T$ | minority carrier lifetime | 0·51 (Ge)<br>0·28 (Si) | 23 (Ge)<br>27·6 (Si) |
| Denney (1954 a) | iron–copper alloy | saturation magnetization | 0·45 | 27 if Fe displaced<br>23 if Cu |
| Eggen and Laubenstein (1953) | copper | resistivity | 0·49 | 25 |
| Dugdale (1955) | $Cu_3Au$ | ordering | ∼ 0·3 | ∼ 10 |

### 14.3. *Amount of Damage*

Very few of the experiments give any reliable estimate of the actual number of displaced atoms, as the theory of the effects produced by one vacancy and one interstitial are not good enough to be used with any certainty, and any effect of clustering is difficult to allow for. The electrical resistivity measurements can be used if the theoretical calculations of Jongenburger (1953) and Blatt (1955) are accepted. This has been done by Harrison and Seitz (1955) using the experimental data obtained by Cooper, Koehler and Marx (1955) for the effect of deuteron irradiation at 10°K. The resulting number of displacements is only one-fifth of the number calculated on the theory of Snyder and Neufeld (1955), while the discrepancy is a factor 7·3 if the resistivity at liquid nitrogen temperature is used. A similar calculation applied to the resistivity change produced in copper by electron bombardment at liquid nitrogen temperature gave a number of defects 5·7 times smaller than the theory. Harrison and Seitz suggest that the uniformity of this discrepancy implies either that the calculations of resistivity of Jongenburger and

Blatt are giving a figure five times too large, or that the Snyder and Neufeld theory is wrong, possibly in its assumption that all atoms which get an energy above the threshold energy are in fact displaced. Blatt, Huse and Rubenstein (1955) have pointed out that a similar calculation of the resistivity caused by small concentrations of gallium, germanium and arsenic in copper give a figure twice that found experimentally, so that the resistivity calculation may well be overestimating by a factor of the order of two, and, if the ideas of Kinchin and Pease (1955 a, b) on the possibility of replacement collisions are added to the Snyder and Neufeld theory, the number of displaced atoms might be lowered by a factor of the order of two, so that the two estimates might be brought into reasonable agreement without having to modify the assumption about the escape of atoms obtaining the threshold energy.

However, the situation is more complex than the resistivity data taken alone would indicate. Overhauser's stored energy measurements (1954) provide another method of estimating the damage stored in deuteron irradiated copper if a value is assumed for the energy stored by one vacancy–interstitial pair. The calculation of this energy seems to be more reliable than that of the resistivity, and taking a value of 5 ev, Overhauser deduced the concentration of pairs in his sample after bombardment with $10^{17}$ deuterons per $\mathrm{cm}^2$ to be $5\times10^{-5}$. As the resistivity of these samples is also known, this gives an independent estimate of the resistivity of a vacancy–interstitial pair, and the value obtained is 11 micro ohm cm per 1% displacements. This is to be compared with 2·7 micro ohm cm per 1% displacements calculated by Jongenburger and Blatt. This estimate therefore indicates that the resistivity calculations are *low* by a factor four, and if this interpretation is accepted, the numbers of defects found in the low temperature irradiation experiment of Cooper, Koehler and Marx would differ from the number calculated by the Snyder and Neufeld theory by a factor of 20. If on the other hand the resistivity calculations of Jongenburger and Blatt are assumed to be right, then the energy stored by a vacancy–interstitial pair would have to be as low as 1·2 ev. To summarize this discussion table 4 collects the possible sets of consistent figures to interpret the results of Cooper, Koehler and Marx. In this table it has been assumed that *all* the additional resistivity is due to vacancies and interstitials. If the fact that one-quarter of Overhauser's additional resistivity did not anneal out at room temperature means that this resistivity is due to some other cause, then the concentration of displaced atoms in the last column should be decreased by about 10%, however as the interpretation of the annealing processes is still in some doubt (e.g. vacancy migration may not have occurred at room temperature) it has been thought as well to leave this uncorrected in the table. At all events, the table shows the limits within which the number of displaced atoms must lie.

Other methods for estimating the amount of damage that have been suggested are as follows. The measurement of lattice parameter (Tucker and Sampson 1955); this again involves a theory of uncertain reliability.

The long wavelength neutron diffraction (Antal, Weiss and Dienes 1955); in this case the theory is straightforward, if the damage consists of simple vacancies and interstitials, but experimental difficulties may prove great as a large specimen will be needed, and production of unclustered defects would then appear to be possible only if gamma radiation were used, when very large doses would be needed; even if clustering were thought not to be serious, the number of materials with small enough neutron capture cross sections is not large.

Table 4. The Possible Consistent Interpretations of the Additional Resistivity of $2{\cdot}1\times 10^{-7}$ ohm cm found by Cooper, Koehler and Marx (1955) after $1{\cdot}1\times 10^{7}$ Deuterons of 12 Mev per cm$^2$ at 10°K. The figures underlined are the results of theoretical calculations by the authors in the first column.

| Author accepted | Resistivity of 1% atoms displaced micro ohm cm | Energy stored by one displaced atom† ev | Concentration of displaced atoms |
|---|---|---|---|
| Huntington (1953) | 11 | 5 | $1{\cdot}9\times 10^{-4}$ |
| Jongenburger (1953), and Blatt (1955) | 2·7 | 1·2 | $7{\cdot}8\times 10^{-4}$ |
| Blatt, Huse and Rubenstein (1955) | 1·3 | 0·6 | $15{\cdot}6\times 10^{-4}$ |
| Snyder and Neufeld (1955) with factor two* | 1·0 | 0·44 | $21{\cdot}5\times 10^{-4}$ |
| Snyder and Neufeld (1955) | 0·49 | 0·22 | $43{\cdot}0\times 10^{-4}$ |

* The factor two is to allow for replacement collisions (Kinchin and Pease 1955 a, b); it also restores the Snyder and Neufeld calculation to very nearly the same value as the original Seitz (1949) calculation.

† Assuming Overhauser's value for the ratio between stored energy and resistivity.

If the theory of James and Lark-Horovitz (1951) has any validity, then the initial rates of carrier removal from high conductivity semiconductors probably gives a good estimate of the number of defects produced. Early results of Crawford and Lark-Horovitz (1950 a, b) and Brattain and Pearson (1950) show that, on these assumptions, 1·5 vacancies are produced per incident fast neutron and 39 per alpha particle, the latest figure (Cleland, Crawford and Pigg 1955) being 2·5 per fast neutron. The amount of radiation damage after long irradiations will be a balance between the new damage produced and annealing effects, whether thermal or radiation-induced.

Table 5. In this Table the Experimental Conditions are Summarized for most of the Experiments referred to in the Text

| Authors | Bombardment | | Total Flux | Bombarded Material | Temperature | Property | Effect |
|---|---|---|---|---|---|---|---|
| | Particle | Energy | Particles/cm$^2$ | | | | |
| Martin, Austerman, Eggleston McGee and Tarpinian (1951) | α | 33 MeV | — | Al and Cu | −150°C, room | Resistivity | Large change if irradiated at −150°C. None if at room temperature |
| Randolph (1952, 1953) | d | 10 MeV | — | Mo | −100°C | Resistivity | Three times if measured at 1·2°K; 4% increase at room temperature |
| Bowen and Rodeback (1953 a, b) | α | 33·6 MeV | $1{\cdot}7\times10^{17}$ | Cu | — | Resistivity and Debye Θ | Debye Θ raised by up to 45° as calculated from resistivity |
| Overhauser (1953 b) | d | 12 MeV | $1{\cdot}1\times10^{17}$ | Cu | −180°C | Resistivity | Change independent of temperature (therefor no change in Debye Θ) |
| Wruck and Wert (1955) | d | 10 MeV | $10^{17}$ | Fe, Ni and Co | −150°C | Resistivity | Larger changes in iron than in the close packed metals |
| Kinchin (Dugdale 1955) | n | pile | $\sim10^{19}$ | W, Mo, Pt | 30°C | Resistivity | ~ 10% change in W, 7% in Mo and 1% in Pt |
| McReynolds, Augustyniak, McKeown and Rosenblatt (1955) | n | pile | $1{\cdot}1\times10^{19}$ | Cu, Al | −150 to −195°C | Resistivity | Increased as measured at −195°C by 20% (Cu), 33% (Al) |
| Cooper, Koehler and Marx (1955) | d | 12 MeV | $1{\cdot}1\times10^{17}$ | Cu, Ag, Au | −261°C | Resistivity | Increase 13% (Cu), 15% (Ag, Au) does not anneal at −261°C |
| Pearlstein, Ingham and Smoluchowski (1955) | p | 100 to 400 MeV | $10^{16}$ | W | room | Resistivity | 0·49% change at 130 MeV, 0·33% at 260 MeV, and 0·71% change at 410 MeV |
| Eggen and Laubenstein (1953) | e | 0·45 to 1 MeV | — | Cu | liq. air | Resistivity | Threshold of electron energy to give effect is 0·49±0·02 MeV implying displacement energy of 25±1 eV |
| Billington and Siegel (1950) | n | pile | $4\times10^{19}$ total | Cu+2wt% Be | 40°C | Resistivity of quenched | Increase 18% |
| Murray and Taylor (1954) | n | pile | $2{\cdot}3\times10^{18}$ total | Cu+13·5 at %Be | — | Resistivity of quenched | Increase 11% |
| Cleland, Billington and Crawford (1953) | n | pile | — | Cu+2wt %Be | −150°C | Resistivity of quenched | Increase one quarter that found at 40°C, but rises to the same value on heating |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Siegel (1949) | n | pile | $3{\cdot}3 \times 10^{10}$ above 50 kev | $Cu_3Au$ | 40°c | Resistivity | Ordered sample increased from 4·6 to $10{\cdot}1 \times 10^{-6}$ ohm cm; disordered gave no change |
| Martin *et al.* (1951) | $\alpha$ | 33 MeV | $3{\cdot}7 \times 10^{17}$ | CuAu and $Cu_3Au$ | −150°c | Resistivity | Ordered samples increased; disordered gave no change |
| Adam and Dugdale (1951) | n | pile | — | $Cu_3Au$ | — | Resistivity | Ordered samples gave initial decrease in resistivity, later increase |
| Glick, Brooks, Witzig and Johnson (1952) | n | pile | $2 \times 10^{20}$ thermal | $Cu_3Au$ | 80°c | Resistivity | Ordered gave rapid drop followed by steady increase to 60% above initial value, disordered gave decrease saturating at 7% below intial and then increasing slowly |
| Glick and Witzig (1953) | n | pile | $1{\cdot}4 \times 10^{20}$ thermal | $Cu_3Au$ | 140°c | Resistivity | Ordered gave 6% drop followed by increase to 4% above initial; disordered gave decrease saturating at 17% below initial. |
| Fillnow, Halteman and Mechlin (1953) | n | pile | $3 \times 10^{20}$ thermal | $Cu_3Au$ | 80°c | Hardness and X-ray lines | Disordered increased from 100 to 121 VPN and gave no X-ray change. Ordered increased from 110 to 158 VPN and X-ray lines sharpened |
| Blewitt and Coltman (1952) | n | pile | $\sim 2{\cdot}1 \times 10^{18}$ | $Cu_3Au$ | 200°c | Resistivity | Lag of 12 hours when pile shut down. This implies relaxation time |
| Coltman and Blewitt (1952) | n | pile | — | $Cu_3Au$ | — | X-ray lines | Imply domain size 125 Å after radiation of ordered alloy. |
| Coltman and Blewitt (1953) | n | pile | $1{\cdot}2 \times 10^{16}$ fast | $Cu_3Au$ | −160°c | Resistivity | Ordered sample gave slight increase, decreasing only on annealing |
| Dixon and Bowen (1954) | $\alpha$ | 36 MeV | — | $Cu_3Au$ | −180°c | Resistivity | Initial rate of disordering six times that at 220°c |
| Adam, Green and Dugdale (1953) | e | 1 MeV | $3 \times 10^{17}$ | $Cu_3Au$ | 40 to 45°c | Resistivity | No change. But anneal at 100°c reduced resistance of ordered |
| Dugdale (1955) | $\gamma$ | $^{60}Co$ | $6 \times 10^{16}$ | $Cu_3Au$ (ordered) | — | Resistivity | Annealing at 128°c for 500 min gives $\rho$ change of $3 \times 10^{-8}$ ohm cm., implying that vacancies have been produced |
| Dugdale (1955) | e | 0·3 MeV | — | $Cu_3Au$ | — | Resistivity | Ordering effect observed, implying that vacancies are produced and that threshold for producing them is below 13·5 eV |
| Dixon, Meecham and Brinkman (1953) | e | 1 MeV | $3 \times 10^{19}$ | $Cu_3Au$ | −195°c | Resistivity | No change. But room temperature anneal gave drop followed by fluctuations |

Table 5 (*continued*)

| Authors | Bombardment |  | Total Flux | Bombarded Material | Temperature | Property | Effect |
|---|---|---|---|---|---|---|---|
|  | Particle | Energy | Particles/cm$^2$ |  |  |  |  |
| Stello (1952) | $\alpha$ | 39·6 MeV | $4{\cdot}1\times10^{17}$ | Cu Au | $<-150$°c | Resistivity | Ordering rates of both ordered and disordered specimens measured at several temperatures |
| Brinkman, Dixon and Meecham (1954) | p | 9 MeV | $5\times10^{17}$ | Cu$_3$Au | $-100$°c | Resistivity | Increased 4·25 $\mu\Omega$ cm if ordered, 0·65 $\mu\Omega$ cm if disordered 0·60 of this anneals before 0°c |
| Cook and Cushing (1953 a, b) | n | pile | $\sim 10^{20}$ | Cu$_3$Au and CuAu | $\sim 30$°c | Resistivity and x-ray lines | Thermal neutrons give ordering of both ordered and disordered. Fast neutrons disorder ordered |
| Eggleston and Bowen (1953) | $\alpha$ | 33 MeV | $2{\cdot}6\times10^{17}$ | $\beta$ brass | $<-100$°c | Resistivity | Increased 100% implying disordering |
| Aronin (1953, 1954) | n | fast | $0{\cdot}9\times10^{20}>\frac{1}{2}$ MeV | Ni$_3$Mn | $\sim 50$°c | Resistivity and magnetic induction | Ordered sample gave increased resistivity and decreased induction. Disordered sample gave decreased resistivity and large increase of induction only if between 16 and 22% Mn |
| Rosenblatt, Smoluchowski and Dienes (1954) | n | pile | 1 week . Brookhaven | $\alpha$ brass | 50°c | Resistivity | Decreased, even as measured at liquid helium temperature. Annealed at 170°c |
| Dugdale (1952, 1955) | n | pile | $4\times10^{18}$ | Pt | $\sim 50$°c | Resistivity and annealing | Increased 0·3%, about 15% of which anneals with $Q=1{\cdot}2$ eV |
| Kinchin (Dugdale (1955) | n | pile | $\sim 10^{19}$ | W, Mo | 30°c | Resistivity annealing | Mo : $Q$ varies from 1·25 to 1·35 eV as 60% of $\rho$ change anneals between 100° and 160°c, and $Q$ is 1·46 eV as 30% anneals 190° to 270°c<br>W : $Q$ varies from 1·2 to 1·6 eV as 20% of $\rho$ change anneals between 70° and 270°c |
| Marx, Cooper and Henderson (1952) | d | 12 MeV | $2{\cdot}7\times10^{17}$ | Cu, Ag, Au Ni, Ta | $-140$°, and $-150$°c | Resistivity and annealing | Changed greatest in Ni and Ta. Recovery observed at $-165$°c with $Q=0{\cdot}15$ eV (Cu, Ag, Au) and 0·20 eV (Ni, Ta) |
| Eggleston (1953 a, b) | $\alpha$ | 35 MeV | $1{\cdot}5\times10^{17}$ | Cu | $-150$°c | Resistivity | Annealing : between $-20$° and $-65$°c $Q=0{\cdot}717$ eV. Between 250° and 350°c $Q=2{\cdot}12$ |
| Overhauser (1953 a, b) | d | 12 MeV | $1{\cdot}1\times10^{17}$ | Cu | $-180$°c | Resistivity | Annealing : below $-60$°c, $Q\propto T$. $-60$°c to room temperature $Q=0{\cdot}68$ eV. Quarter of total change remains at 167°c |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| McReynolds *et al.* (1955) | n | pile | $1{\cdot}1\times10^{19}$ | Cu, Al | −150° to −195°C | Resistivity | Anneals in two processes, −80° to 20°C and, with critical shear stress 300° to 400°C in copper. Anneals with critical shear stress from −80° to −20°C in aluminium |
| Overhauser (1954) | d | 12 MeV | $10^{17}$ | Cu | −150°C | Energy released | Annealing to room temperature releases 1·2 calories per gram |
| Cooper, Koehler and Marx (1954) | d | 12 MeV | $10^{17}$ | Cu, Ag, Au | −261°C | Resistivity | In Cu about 40% of the additional resistivity anneals at −233°C, in Ag 20% at −243°. In Au no sudden drop occurs |
| Andrade (1945, 1953) | α | 5·3 MeV | $1{\cdot}5\times10^{8}$ per sec | Cd single crystals | — | Creep rate | Accelerated by up to ×5 during transient creep only |
| Makin (1954, 1955) | α | 5·3 MeV | $5\times10^{8}$ per sec | Cd single crystals | room | Creep | No effect. If bombardment for 1–2 hrs. precedes creep test, creep rate is reduced ~ 30% |
| Schmid and Lintner (1954 a, b) | α, n | 5·3 MeV | — | Zn single crystals | — | Creep | Hardening, i.e. slower creep. Neutrons seem to produce reverse effect |
| Jones, Munro and Hancock (1954) | n | pile | $1{\cdot}3\times10^{12}$ above 1 eV, per sec | Al polycrystal | 50°C | Creep rate | No change |
| Jeppson, Mather, Andrew and Yockey (1955) | α | 38 MeV | $1{\cdot}2\times10^{13}$ per sec | Al polycrystal | 150° to 320°C | Creep rate | No significant change |
| Witzig (1951, 1952 b) | d | 16 MeV | $10^{12}$ per sec | Cu polycrystal | 260°C | Creep rate | At 10 000 lb/in², no effect to ±20% |
| Billington and Siegel (1950) | n | pile | $5\times10^{19}$ | Cu | 40°C | Hardness | Annealed: RF43 became RF90.<br>Cold worked: RF93 became RF97 |
| Geib and Grace (1952 a, b)<br>Harmon *et al.* (1953) | d | 8·4 to 10 MeV | $1{\cdot}5\times10^{17}$ | Mo | — | Hardness | Increased from 201 to 253 VPN |
| Dixon and Meechan (1953) | c | 1 MeV | $5\times10^{18}$ | Cu | −20°C | Hardness | Increased from 44·7 to 47·7 VPN |
| Murray and Taylor (1953, 1954) | n | pile | $2{\cdot}3\times10^{18}$ | Cu alloys | — | Hardness | Increased ~ 20 VPN for solid solutions, ~ 40 VPN for Cu–Be |
| Fillnow, Halteman and Mechlin (1953) | n | pile | $3\times10^{20}$ | $Cu_3Au$ | 80°C | Hardness | Disordered: 100 to 121 VPN<br>Ordered: 110 to 158 VPN |
| Blewitt and Coltman (1951) | n | pile | $1{\cdot}8\times10^{18}$ fast | Cu single crystal | — | Critical shear stress | Increased from 0·24 to 1·94 Kg mm$^{-2}$ |
| Jamison and Blewitt (1952) | n | pile | $8\times10^{18}$ fast | Cu single crystal | — | Slip lines | More clustered |
| Jamison and Blewitt (1953 a) | n | pile | — | Cu single crystal | — | Stress–strain curve | Measured at 78°K: Critical shear stress raised higher but work hardening lower |

Table 5 (*continued*)

| Authors | Bombardment | | Total Flux | Bombarded material | Temperature | Property | Effect |
|---|---|---|---|---|---|---|---|
| | Particle | Energy | Particles/cm$^2$ | | | | |
| Redman, Coltman and Blewitt (1953) | n | pile | — | Cu single crystal | — | Critical shear stress | Annealing (after rise to 3·5 Kg mm$^{-2}$) in region 300° to 400°. Activation energy 2·2 eV |
| McReynolds *et al.* (1955) | n | pile | $1{\cdot}1 \times 10^{19}$ | Cu, Al | −195°C | Critical shear stress | Raised by factor 5. Anneals ~ 320°C in Cu, −80° to −20°C in Al. $Q=2$ eV (Cu), 0·55 eV (Al) |
| Kunz and Holden (1954 b) | n | pile | $10^{18}$ | Fe, Zn, Pb | room | Yield strength | Increase by ~ ×2 in Fe and Zn crystals. No effect in Pb. Annealing in Fe has $Q=3{\cdot}1$ eV |
| Kelly (1954, 1955) | — | 39·6 MeV | $9 \times 10^{16}$ | Al | −100°C | Slip planes | More slip on a given plane |
| Bruch, McHugh and Hockenbury (1954, 1955) | n | pile | 1·9 to $5{\cdot}9 \times 10^{20}$ | Mo | — | Stress–strain curve | Ductile–brittle transition raised from −30° to +70°C |
| Makin (private communication) | n | pile | $5 \times 10^{19}$ | Ni, Cu, Mo, Ti, etc. | 100°C | Stress–strain curve | Yield stress raised by from 7% to 100%. Elongation and initial hardening rate lowered. Annealing of yield point 300–360° in Cu ($Q=2{\cdot}05$ eV) and 340–400°C in Ni ($Q=2{\cdot}63$ eV) |
| Meyer (1954) | d | 18·6 MeV | $3{\cdot}7 \times 10^{17}$ | SAE 1019 steel | — | Notch sensitivity, hardness | Ductile brittle transition raised from −1° to +18°C. Hardness increased from 180–380 Knoop nos., and depends on penetration. Effect anneals between 260° and 480°C with variable $Q$ |
| Steele and Wallace (1954) | n | pile | $1{\cdot}3 \times 10^{21}$ total<br>~ $10^{20}$ fast | Al alloys | 65°C | Stress–strain curve | Yield stress and U.T.S. increased ~ ×2 for annealed specimens. Elongation decreased ~ 20% |
| Sutton and Leeser (1955 a) | n | pile | $10^{20}$ | steels, Ni and Co alloys, Zr | 20° to 250°C | Hardness, stress–strain curve, notch sensitivity | Rises in hardness ~ 20–150%, yield strength 10–60%, U.T.S. 5–40%. Ductile-brittle transition temperature raised |
| Li and Nowick (1955) | n | pile | — | Cu 17 at % Al | −195° and 50°C | Internal friction | No change |
| Charlesby, Hancock and Sansom (1955) | n | pile | ~ $10^{19}$ | austenitic steel | 60° to 70°C | Elastic modulus | No change |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Kunz and Holden (1954 a, b) | n | pile | $2 \cdot 4 \times 10^{18}$ | copper | — | Elastic constants | No change |
| Dieckamp and Crittenden (1954) | d | 20 Mev | $9 \times 10^{16}$ | Cu | −175°C | Shear modulus | Decreased 1·5%. One-third of this anneals at −125°C, the rest between −50° and +100°C |
| Dieckamp (1955) | e | 1 Mev | $4 \cdot 5 \times 10^{18}$ | copper | −195°C | Shear modulus | Annealing at −50°C gave 4% inc., at 75° gave ½% dec., and at 250° to 350°C a 2% dec. |
| Fleeman and Dienes (1955) | n | pile | $10^{18}$ | β Sn | −195°C | Transformation | Growth of α Sn on heating much faster than unirradiated, but slower than seeded |
| Denney (1953, 1954 a) | e | ~ 0·5 Mev | — | Cu 2·4 wt%Fe | — | Saturation Magnetization | Energy threshold at 0·45 Mev for transformation, implying displacement energy of 27±2 ev for Fe |
| Denney (1954 b) | p | 9 Mev | — | Cu 2·4 wt%Fe | — | Saturation Magnetization | When fully precipitated before irradiation magnetization drops implying local melting |
| Warren (1951, 1952, 1953) | n | pile | 6 Months Hanford | Cu, Zr, Ge, Al | — | X-ray lines | No effect |
| Warren (1954) | n | pile | 550 Mwd/at. | Cu 2% Si single crystal | — | X-ray lines | No change, but subsequent etch gives very broad peaks |
| Adam (Dugdale 1955) | n | pile | $1 \cdot 5 \times 10^{19}$ fast | Pt, Mo | — | X-ray lines | No change in Pt, 1 : 10 000 inc. in lattice spacing in Mo |
| Kunz and Holden (1954 a, b) | n | pile | ~ $10^{18}$ | Cu, Mg, brass | — | X-ray lines | Line broadening in all, and shift in brass |
| Adam (private communication) | n | pile | ~ $10^{19}$ | $WAl_5$ | — | X-ray lines | Indicated expansion of 0·1% in $c$ direction, and a slight contraction in the $a$ direction |
| Kierstead (1955) | d | 19 Mev | $1 \cdot 15 \times 10^{17}$ | copper | −195°C | Volume | 0·034% increase. 14% of this anneals by room temperature, but radiation at room temp. gives only 0·1% volume change |
| Johnson and Martin (1952) | p | 10 Mev | $3 \times 10^{14}$ per sec | Ag | — | Self diffusion | No measurable change |
| Callendine, Ridolfo and Pool (1952) | n | pile | — | Co, Au plated | — | Diffusion | Some Co appears to have been knocked through the gold layer |
| Andrew, Jeppson and Yockey (1952) | α | 40 Mev | — | Fe, Pt etc. | — | Thermo e.m.f. | No change to $3 \times 10^{-7}$ volt/°C |
| Jamison and Blewitt (1953 b) | n | pile | $5 \times 10^{16}$ | Cu and Fe-constantan | — | Thermo e.m.f. | No change to $10^{-5}$ volt between liquid nitrogen and ice temperature |
| Andrew and Davidson (1953) | p | 10 Mev | $5 \times 10^{17}$ | Fe | — | Thermo e.m.f. | ~ 0·3 μV per °C between irradiated and unirradiated iron |

Table 5 (*continued*)

| Authors | Bombardment | | Total Flux | Bombarded Material | Temperature | Property | Effect |
|---|---|---|---|---|---|---|---|
| | Particle | Energy | Particles/cm$^2$ | | | | |
| Andrew and Davidson (1953) | p | 10 MeV | $3{\cdot}8 \times 10^{17}$ | Constantan | — | Thermo e.m.f. | $\sim 0{\cdot}1\ \mu$V per °C between irradiated and unirradiated constantan |
| Lark-Horovitz, Bleuler, Davis and Tendam (1948) | d | 10 MeV | — | Ge | — | Resistivity | Pure and p-type: decreased. n-type became p-tpye |
| Johnson and Lark-Horovitz (1949) | n | fast | 1 day ORNL | Ge | — | Resistivity | p-type: decreased. n-type; increased to maximum when it changed to p-type and decreased |
| Lark-Horovitz, Becker, Davis and Fan (1950) | n | fast | — | Si | — | Resistivity | Increased in all cases to over 10 000 ohm cm |
| Fan (1952), Fan and Becker (1951), Becker, Fan and Lark-Horovitz (1952) | n | fast | — | Si | — | Absorption bands | New band and decrease in long wavelength absorption imply introduction of electron and hope traps |
| Crawford and Lark-Horovitz (1950 a, b) | n | fast | — | Ge | — | No. of holes per n | n-type: 3 per fast neutron, p-type: 0·7 per fast neutron |
| Brattain and Pearson (1950) | $\alpha$ | 5·3 MeV | $4{\cdot}5 \times 10^{10}$ | Ge | room | Resistivity | n-type becomes p-type. Initially losing 78 electrons per $\alpha$, after conversion gaining 8·6 holes per $\alpha$. |
| Crawford, Cleland, Lark-Horovitz, Pigg and Young (1952) | n | fast | $1{\cdot}2 \times 10^{16}$ | Ge | — | Resistivity | Low resistivity p-type: increased on bombardment |
| Forster, Fan and Lark-Horovitz (1952) | d | 10 MeV | — | Ge and Si | — | Carriers lost per d | Low resistivity p-type Ge: 4, n-type Ge: 11, p-type Si: 31 |
| Klontz (1943 a) | e | 0·4 to 1·5 MeV | $\sim 10^{18}$ | Ge | $-196$°C | Threshold energy | 0·65 MeV for permanent resistivity charge. Implies displacement energy 30 eV |
| Loferski and Rappaport (1955) | e | 0·3 to 1·5 MeV | — | Ge and Si electron voltaic cells | room | Short circuit current | Rise of current with bombardment time if electrons above threshold energy of 0·51 MeV (Ge), 0·28 MeV (Si). This implies displacement energies of 23 eV (Ge), 27·6 eV (Si) |
| Klontz (1953 b) | e | 4·2 MeV | $\sim 4{\cdot}5 \times 10^{9}$ | Ge | $-196$°C | Resistivity and annealing | p-type of 2·18 ohm cm initial resistivity: reduction of conductivity annealing at room temperature |
| Cussins (1951) | ions $^1$H to $^{51}$Sb | 5 to 90 keV | | Ge | — | Diode characteristics | Effects produced consistent with production of p-type surface layer |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Foster, Fan and Lark-Horovitz (1953) | d | 9·3 MeV | — | Ge | −170°c | Hall coefft. and resistivity | Annealing at <141°K both $R$ and $\rho$ increase, above 141°K they decrease |
| Crawford, Cleland, Holmes and Pigg (1953) | n | pile | — | Ge | −90° to −160°c | Hall coefft. and resistivity | Annealing at <140°K gives increase of resistivity with first order process |
| Pepper, Klontz, Lark-Horovitz and McKay (1954) | e | 4·5 MeV | — | Ge | −186°c | Hall coefft. and resistivity | p-type (In doped) $R$ and $\rho$ both increase $R/\rho$ constant. (Au doped) $R$ and $\rho$ decrease $R/\rho$ goes through minimum of one third its intial value. n-type: $R$ and $\rho$ both increase, $R$ passes through maximum negative value and later becomes positive |
| Klonz, Pepper and Lark-Horovitz (1955) | e | 4·5 MeV | — | Ge | −186°c | Resistivity and Hall coefficient | $R$ and $\rho$ both increase in both types. Annealing studied |
| Taylor, Odell and Fan (1952) | n | — | — | n-Ge | — | Grain boundary barrier | High resistance eliminated when n-type converted to p-type |
| Brown, Fletcher and Wright (1953) | e | 3 MeV | $10^{14}$ | n-Ge | — | Resistivity annealing | Fits theory. Activation energy from second part of process is 1·8 eV |
| Pigg, Cleland, Crawford, and Lark-Horovitz (1951) | n | pile | — | $Cu_2O$ | — | Resistivity | Increased |
| Odencrantz (1952) | α | 5·3 MeV | | PbS | — | Resistivity | Increased to three times after initial drop of a few per cent |
| Keesom, Lark-Horovitz and Pearlman (1952 a, b, 1953) | n | pile | — | Si | — | Specific heat | Linear contribution much reduced by bombardment and Debye $\Theta$ reduced |
| Cleland and Crawford (1954 a, b, c) | n | pile | — | In Sb | 30°c | Hall coefficient | p-type became n-type, n-type tends to high resistivity n-type |
| Cleland and Crawford (1955) | n | pile | — | GaSb | — | Resistivity and Hall coefficient | Both n- and p-type increase in resistivity, and Hall measts. show carrier traps are formed, though the rate of removal varies with initial concentration in p-type but not n-type |
| Kinchin (1954) | n | pile | $5\times10^{19}$ thermal | Graphite | 30°c | Resistivity Hall coefficient and magneto-resistance | Resistivity and Hall coefficient increase, magneto resistance drops. Effects consistent with production of electron traps |
| Stevens, Clelland and Crawford (1954), Stevens (1954) | n | pile | — | n-Ge | — | Magnetic susceptibility | Decreased the diamagnetism |
| Schulz-DuBois, Nisenoff, Fan and Lark-Horovitz (1955) | n | pile | — | p-type B doped Si | — | Electron spin resonance | Observed only in irradiated specimens |
| Weissman and Chang (1955) | n | pile | $1\cdot4\times10^{18}$ slow<br>$1\cdot2\times10^{18}$ fast | Ge single crystals | 160° to 200°c | x-ray lines | $\frac{1}{2}$-widths increased from 36″ to $3\frac{1}{2}'$. Diffuse scattering increased and $a_0$ raised from $5\cdot657_7$ to $5\cdot659_2$ Å |

Table 5 (*continued*)

| Authors | Bombardment | | Total Flux | Bombarded material | Temperature | Property | Effect |
|---|---|---|---|---|---|---|---|
| | Particle | Energy | Particles/cm$^2$ | | | | |
| **Keating (1955 b)** | n | pile | $2{\cdot}1\times10^{19}$ | Graphite | −196°C | X-ray lines | $c_0$ increased 4·75%. X-ray reflections broaden and have longer tails |
| Vaughan, Leivo and Smoluchowski (1953) | p | 400 MeV | — | NaCl | — | Hardness and Elasticity | Increased from 16·3 to 36 VPN. Young's modulus also increased |
| Westervelt (1953, 1954) | x<br>e<br>α | —<br>1 MeV<br>40 MeV | — | Alkali halides | 20°C<br>20°C<br>−170°C | Hardness<br>Hardness<br>Hardness | Increased from 16·3 to 33·4 VPN (NaCl)<br>Increased from 16·3 to 36 VPN (NaCl)<br>Increased from 16·3 to 46 VPN (NaCl) |
| Frankl and Read (1953) | x | — | — | NaCl | — | Internal friction | Reduced |
| Gordon and Nowick (1955) | x | — | — | NaCl | — | Elastic modulus | Increased in cold worked specimens to annul decrease caused by the work |
| Binder and Sturm (1954 b) | n | pile | $6\times10^{16}$ | LiF | — | Lattice parameter and density | Changes equivalent to within 6% |
| Keating (1955) | n | pile | $7{\cdot}5\times10^{17}$ | LiF | — | Lattice parameter | No change. But X-ray line broadening |
| Warren (1952, 1953) | n | pile | 8 days Argonne | LiF | — | X-ray spots | Broadened and intensified |
| Berry (1955) | x | — | — | KCl | — | Lattice parameter | Increase in $a_0$ of 0·001% |
| Primak, Delbecq and Yuster (1955) | x or d | —<br>21 MeV | —<br>$10^{13}$ | LiF | — | Density from birefringence | Decreased 2 to $9\times10^{-5}$ |
| Leivo and Smoluchowski (1954) | p | 400 MeV | $5\times10^{15}$ | KCl | — | Density | Decreased by $2\times10^{-4}$ gm cm$^{-3}$ |
| Smith, Leivo and Smoluchowski (1954) | x or p | — | — | KCl | — | Surface | Slip lines in irradiated area. X and p effects similar except at high p doses |
| Lin and Russell (1955) | x | — | — | KCl and NaCl | — | Change of length | Agrees to within 5% with optical determination of colour centre density |
| Primak (1954) | n | pile | — | various covalent compounds | — | X-ray powder patterns | Effects vary from none to large from substance to substance |
| Hurley and Fairburn (1952, 1953) and Holland and Gottfried (1955) | α | — | $10^{16}$ per mg | Zircon | — | X-ray pattern | Line intensity decreases reaching background at $10^{16}\alpha$ per mg |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Wittels (1953) | n | pile | $6{\cdot}6\times10^{19}$ fast | Quartz | — | Lattice | Becomes more anisotropic, density decreased 3·5% |
| Wittels and Sherrill (1954) | n | pile | $2\times10^{20}$ fast | $SiO_2$, various structures | — | Structure | All turn to a glass which on heating recrystallizes to quartz |
| Johnson and Pease (1954) | n | pile | $10^{19}$ | Quartz oscillators | — | Frequency and bleaching | Frequency decreases linearly with dose. X-rays no longer colour crystal |
| Pease (1954) | n | pile | $10^{18}$ thermal | BN and other B compounds | — | Lattice parameter and X-ray lines | Changes ~1% in lattice parameter which saturate with dose. Lines broaden, some reaching saturation and some not |
| Tucker and Senio (1954, a, b, 1955 a, b) | n | pile | $3\times10^{20}$ thermal | $B_4C$ | — | Lattice parameter and X-ray lines | Contraction in $c$ and expansion in $a$, heavy diffuse spots |
| Hayes and Smoluchowski (1953) | p | 360 MeV | — | Diamond | — | X-ray pattern | Scattering angle increased 10′ to 30′ |
| Robinson, Li and Smoluchowski (1954) | p | 360 MeV | — | Diamond | — | X-ray pattern | Unexpected weak maximum at 0·02 radian |
| Mapother (1953) | x | — | — | NaCl | <550°C | Diffusion | Decreased |
| Nelson, Sproull and Caswell (1953) | $\gamma$<br>n | $^{60}$Co<br>pile | — | KCl | — | Electrical conductivity | Short $\gamma$ irradiation gives decrease, long $\gamma$ or n irradiation gave increase |
| Pearlstein (1953 a, b, 1954, also Smoluchowski 1955) | p<br>$\gamma$ | 400 MeV<br>MsTh | $10^{14}$ to $10^{17}$ | KCl and NaCl | — | Electrical conductivity | Small bombardment: decrease; long bombardment: increase. Annealing gives large decrease followed by increase |
| Berman (1951) | n | pile | $2\times10^{19}$ fast | Quartz | — | Thermal conductivity | Peak at 12°K disappears and conductivity is more like that of a glass |
| Berman, Foster and Rosenberg (1955) | n<br>$\gamma$ | pile<br>— | $5\times10^{18}$<br>— | Artificial sapphire | — | Thermal conductivity | Much reduced at low temperatures |
| McClelland and Donoghue (1953) | n | pile | $3{\cdot}8\times10^{19}$ fast | Oxides | — | Magnetic susceptibility | Many become less diamagnetic |
| Stevens (1955) | n | pile | $5\times10^{19}$ fast | Quartz | — | Magnetic susceptibility | Independent of $T$ before irradiation, decreases with decreasing $T$ after. Further irradiation reduces effect |
| Duhamel, Freymann and Freyman (1953) | n | pile | $1{\cdot}8\times10^{16}$ | ZnO | — | Absorption of electro-magnetic radiation | Noticeable changes |
| Griffiths, Owen and Ward (1955) | n | pile | — | Quartz<br>Diamond | — | Paramagnetic resonance | Lines found. In quartz their fine structure shows ‘smoky’ coloration is due to Al |

The distribution of the damage must also be considered. In general it will be highly inhomogeneous because the damage is grouped round the positions where the incident particles make their collisions. The volume of a thermal spike can be estimated from the disordering effects, the volume disordered by one neutron containing about $10^4$ atoms (Cook and Cushing 1953 a, b, Aronin 1954).

### 14.4. *Annealing of the Damage*

As this subject has been discussed at length in § 7, we shall here only summarize the main conclusions reached. The various combinations of vacancies and interstitials can recombine if supplied with differing activation energies. Close vacancy interstitial pairs (or possibly local melt zones on the thermal spike picture) almost certainly are the most easily removed form of damage in metals, and can be annealed at liquid air temperature. The activation energy will depend on the separation, so that the annealing curve will correspond to the sum of several monomolecular reactions.

The next easiest process is interstitial migration, though if caterpillars (crowdions) can exist, they may get trapped by vacancies on another close packed line instead of being annihilated. No reliable calculations for this process exist. Clusters of vacancies are not likely in lightly electron damaged samples, but may be found in more heavily damaged samples, or samples that have suffered thermal spikes ; these will probably move next.

Vacancy migration may occur at either 0·7 ev or 1·2 ev, it may be hindered by the trapping of vacancies on impurity atoms, and after it is operating, recovery may be accelerated by the formation of vacancy pairs.

Finally, when self-diffusion is possible, any dislocations produced by thermal strains can climb and either disappear or at least polygonize. In copper this occurs with an activation energy of about 2·1 ev.

Unfortunately many of the above statements are speculative, and we are still far from a full understanding of the annealing of point defects in metals. Experiments on quenched specimens (which should contain only vacancies) and using precision lattice parameter measurements (which should be more sensitive to interstitials than vacancies especially if the interstitials are not crowdions) may help to sort out the confusing number of possibilities portrayed in table 2. Until these experiments are performed it will not be possible to state what the state of radiation damage is at any temperature above 50°K even in the most studied metal, copper.

In metals of differing type, such as aluminium, where closed shell repulsions are much less important, and iron, with its body-centred cubic structure, the relative activation energies for the movement of defects, the geometry of the clusters produced and even the nature of the individual interstitialcy, may be quite different, and much work will have to be done on comparative studies of different metals before the theory of the annealing of radiation damage can be presented with any certainty.

## ACKNOWLEDGMENTS

I should like to thank many friends both at Harwell and Cambridge for helpful discussions and criticisms of parts of this paper. Particular thanks are due to Dr. M. J. Makin and Mr. J. Adam for permission to quote as yet unpublished data.

## REFERENCES

(A) after a reference indicates that it is a reference to an abstract of a conference paper.

ABELÈS, F., 1953, Résistance électrique et pouvoir thermoélectrique supplémentaires dus aux lacunes dans les métaux. *Comptes Rendus Acad. Sci.*, **237,** 796.

ADAM, J., and DUGDALE, R. A., 1951, Some experimental work carried out in physics with the larger Harwell pile. *Nature, Lond.*, **168,** 581.

ADAM, J., GREEN, A., and DUGDALE, R. A., 1952, An effect of electron bombardment on order in $Cu_3Au$ alloy. *Phil. Mag.* (7), **43,** 1216.

ANDRADE, E. N. da C., 1945, Effect of alpha-ray bombardment on glide in metal single crystals. *Nature, Lond.*, **156,** 113 ; 1953, The effect of surface conditions on the mechanical properties of metals, mainly single crystals. *Monogr Ser. Inst. Metals*, No. 13, 133.

ANDREW, A., and DAVIDSON, C. R., 1953, Induced thermoelectric potential from radiation damage. *Phys. Rev.* (2), **89,** 876.

ANDREW, A., JEPPSON, M. P., MATHER, R. L., and YOCKEY, H. P., 1954, The creep of aluminum under cyclotron irradiation. *Phys. Rev.* (2), **96,** 843, (A).

ANDREW, A., JEPPSON, M. R., and YOCKEY, H. P., 1952, Effect of cyclotron irradiation on some thermocouple materials. *Phys. Rev.* (2), **86,** 643, (A).

ANTAL, J. J., WEISS, R. J., and DIENES, G. J., 1955, Long wavelength neutron transmission as an absolute method for determining the concentration of lattice defects in crystals. *Phys. Rev.* (2), **98,** 1541, (A).

ARONIN, L. R., 1953, Radiation damage effects on order–disorder in nickel–manganese alloys. U. S. Report AECU-2634 ; 1954, Radiation damage effects on order–disorder in nickel–manganese alloys. *J. Appl. Phys.*, **25,** 344.

BARNES, R. S., and MAKIN, M. J., 1955, On the mechanism of irradiation annealing. British Report AERE M/R 1626, 9 p.

BARTLETT, J. H., and DIENES, G. J., 1953, Combined pairs of vacancies in copper. *Phys. Rev.* (2), **89,** 848.

BECKER, M., FAN, H. Y., and LARK-HOROVITZ, K., 1952, Infrared absorption of nucleon-bombarded silicon I. *Phys. Rev.* (2), **85,** 730, (A).

BERMAN, R., 1951, The thermal conductivities of some dielectric solids at low temperatures. *Proc. Roy. Soc.* A, **208,** 90.

BERMAN, R., FOSTER, E. L., and ROSENBERG, H. M., 1955, The thermal conductivity of irradiated dielectric crystals at low temperatures. *Report of the Conference on Defects in Crystalline Solids*, Bristol, 1954 (London : Physical Society), p. 321.

BERMAN, R., KLEMENS, P. G., SIMON, F. E., and FRY, T. M., 1950, Effect of neutron irradiation on the thermal conductivity of a quartz crystal at low temperature. *Nature, Lond.*, **166,** 864.

Berry, C. R., 1955, Changes in KCl lattice dimensions by soft x-rays. *Phys. Rev.* (2), **98,** 1540, (A).

Billington, D. S., and Siegel, S., 1950, Effect of nuclear radiation on metal. *Metal Progress,* **58,** 847 ; see also U.S. Report AECD-2810.

Binder, D., and Sturm, W. J., 1954 a, On the equivalence of x-ray lattice parameter and density changes in neutron irradiated LiF. *Phys. Rev.* (2), **94,** 760, (A) ; 1954 b, Equivalence of x-ray lattice parameter and density changes in neutron irradiated LiF. *Ibid.* (2), **96,** 1519.

Binnie, W. P., and Liebschutz, A. M., 1952, An x-ray and electron diffraction study of radiation damage in single crystals. U.S. Report AECU-2225, 4 ; 1953 a, An x-ray and electron diffraction study of radiation damage in single crystals of germanium and silicon. U.S. Report COO-102, 15 ; 1953 b, An x-ray study of radiation damage in single crystals. U.S. Report COO-104, 41 ; 1954, The elastic constants of silicon before and after neutron bombardment from x-ray diffuse scattering, *Phys. Rev.* (2), **94,** 1410, (A).

Blatt, F. J., 1955, Effect of vacancies and interstitials on the electrical properties of copper. *Phys. Rev.* (2), **98,** 245, (A).

Blatt, F. J., Huse, M. C., and Rubenstein, R. A., 1955, On the resistance due to point imperfections in copper. *Phys. Rev.* (2), **98,** 1553, (A).

Blewitt, T. H., and Coltman, R. R., 1951, The effect of pile irradiation on the stress–strain curve of copper. *Phys. Rev.* (2), **82,** 769, (A) ; 1952, The effect of neutron irradiation on metallic diffusion. *Ibid.* (2), **85,** 384 ; 1955, Radiation ordering in $Cu_3Au$. *Acta Metallurgica,* **2,** 549.

Bowen, D. B., Eggleston, R. R., and Kropschot, R. H., 1952, A study of the annealing kinetics in cold-worked copper. *J. Appl. Phys.,* **23,** 630.

Bowen, D. B., and Rodeback, G. W., 1953 a, The influence of cold work and radiation damage on the vibrational spectra of copper. *Phys. Rev.* (2), **92,** 531, (A) ; 1953 b, The influence of cold work and radiation damage on the Debye temperature of copper. *Acta Metallurgica,* **1,** 649 ; see also U.S. Report NAA-SR-254, 17 p.

Brattain, W. H., and Pearson, G. L., 1950, Changes in conductivity of germanium produced by alpha-particle bombardment. *Phys. Rev.* (2), **80,** 846.

Bredig, M. A., Klein, G. E., and Borie, B. S., Jr., 1955, x-ray diffractometer for highly radioactive materials. *Rev. Sci. Instrum.,* **26,** 610.

Brinkman, J. A., 1952, On the nature of radiation damage in metals. U.S. Report NAA-SR-198 ; 1954, On the nature of radiation damage in metals. *J. Appl. Phys.,* **25,** 961.

Brinkman, J. A., Dixon, C. E., and Meechan, C. J., 1953, Interstitial and vacancy migration in $Cu_3Au$ and copper. U.S. Report NAA-SR-249 ; 1954, Interstitial and vacancy migration in $Cu_3Au$ and copper. *Acta Metallurgica,* **2,** 38.

Broom, T., 1954, Lattice defects and the electrical resistivity of metals. *Advances in Physics,* **3,** 26.

Brown, W. L., and Fletcher, R. C., 1953, Annealing of bombardment damage in germanium : experimental, *Phys. Rev.* (2), **91,** 237, (A).

Brown, W. L., Fletcher, R. C., and Machlup, S., 1953, Annealing of bombardment damage in solids. *Phys. Rev.* (2), **90,** 709.

Brown, W. L., Fletcher, R. C., and Wright, K. A., 1953, Annealing of bombardment damage in germanium : experimental. *Phys. Rev.* (2), **92,** 591 ; 1954, Traps produced by electron bombardment of germanium at low temperature. *Ibid.* (2), **96,** 834, (A).

Bruch, C. A., McHugh, W. E., and Hockenbury, R. W., 1954, Embrittlement of molybdenum by neutron radiation. U.S. Report KAPL-1095, 54 p ; 1955, Embrittlement of molybdenum by neutron radiation. *J. Metals*, **7,** 281.

Bueren, H. G. van, 1955, Elektrischer Widerstand und plastische Deformation von Metallen. *Zeit. Metallk.*, **46,** 272.

Calkins, V. P., 1954 a, Radiation effects on reactor materials : non-metals. *Nucleonics*, **12,** 9, 9 ; 1954 b, Radiation effects on reactor materials : non-metals. *Nuclear Engineering*, Part II, Chem. Eng. Progr. Symposium Ser., 50, 12, 28.

Callendine, G. W., Jr., Ridolfo, V. C., and Pool, M. L., 1952, Diffusion effects of cobalt when bombarded with neutrons. *Phys. Rev.* (2), **86,** 642, (A).

Charlesby, A., Hancock, N. H., and Sansom, H. C., 1954, Effect of atomic pile radiation on the elastic modulus of an austenitic steel. British Report AERE M/R 1434 ; 1955, Effect of atomic-pile radiation on the elastic modulus of an austenitic steel. *J. Nuclear Energy*, **1,** 264.

Chipman, D. L., Warren, B. E., and Dienes, G. J., 1953, x-ray measurements of radiation damage in black phosphorus, *J. Appl. Phys.*, **24,** 1251 ; see also U.S. Report BNL-1479.

Cleland, J. W., Billington, D. S., and Crawford, J. H., Jr., 1953, Low temperature fast neutron bombardment of copper–beryllium alloy. *Phys. Rev.* (2), **91,** 238, (A).

Cleland, J. W., and Crawford, J. H., Jr., 1954 a, Radiation effects in indium antimonide. *Phys. Rev.* (2), **93,** 894 ; 1954 b, Radiation effects in indium antimonide. *Ibid.* (2), **94,** 1410, (A) ; 1954 c, Neutron irradiation of indium antimonide. *Ibid.* (2), **95,** 1177 ; 1955, Radiation effects in gallium antimonide. *Ibid.* (2), **99,** 637, (A).

Cleland, J. W., Crawford, J. H., Jr., Lark-Horovitz, K., and Pigg, J. C., 1951, The effect of fast neutron bombardment on the conductivity of P-type germanium. *Phys. Rev.* (2), **82,** 763, (A).

Cleland, J. W., Crawford, J. H., Jr., Lark-Horovitz, K., Pigg, J. C., and Young, F. W., Jr., 1951 a, The effect of fast neutron bombardment on the electrical properties of germanium. *Phys. Rev.* (2), **83,** 312 ; 1951 b, Evidence for the production of hole traps in germanium by fast neutron bombardment. *Ibid.* (2), **84,** 861.

Cleland, J. W., Crawford, J. H., Jr., and Pigg, J. C., 1955, Fast-neutron bombardment of *n*-type Ge. *Phys. Rev.* (2), **98,** 1742.

Coltman, R. R., and Blewitt, T. H., 1952, The effect of neutron irradiation of [sic] metallic diffusion. *Phys. Rev.* (2), **86,** 641, (A) ; 1953, The effect of fast neutron bombardment on diffusion in $Cu_3Au$. *Ibid.* (2), **91,** 235, (A).

Cook, L. G., and Cushing, R. L., 1953 a, The effects of neutron irradiation in the NRX reactor on the order–disorder alloy $Cu_3Au$. *Acta Metallurgica*, **1,** 539 ; 1953 b, The effects of neutron irradiation in the NRX reactor on the order–disorder alloy CuAu. *Ibid.*, **1,** 549.

Cooper, H. G., Koehler, J. S., and Marx, J. W., 1954, Resistivity changes in copper, silver and gold produced by dueteron irradiation near 10°K. *Phys. Rev.* (2), **94,** 496 ; 1955, Irradiation effects in Cu, Ag and Au near 10°K. *Ibid.* (2), **97,** 599.

Crawford, J. H., Jr., Cleland, J. W., Holmes, D. K., and Pigg, J. C., 1953, Thermally unstable disorder in p-type Ge produced by fast neutron bombardment. *Phys. Rev.* (2), **91,** 243, (A).

Crawford, J. H., Jr., Cleland, J. W., Lark-Horovitz, K., Pigg. J. C., and Young, F. W., Jr., 1952, Evidence of hole traps in Ge produced by fast neutron bombardment. *Phys. Rev.* (2), **85,** 730, (A).

Crawford, J. H., Jr., and Lark-Horovitz, K., 1950 a, Fast neutron bombardment effects in germanium. *Phys. Rev.* (2), **78,** 815 ; 1950 b, Thermal equilibrium in neutron irradiated semiconductors. *Ibid.* (2), **79,** 889.

Cummings, W. V., Jr., Kaulitz, D. C., and Sanderson, M. J., 1955, Double diffracting x-ray spectrometer for study of irradiated materials. *Rev. Sci. Instrum.,* **26,** 5.

Cussins, W. D., 1955, Effects produced by the ionic bombardment of germanium. *Proc. Phys. Soc.* B, **68,** 213.

Davis, R. E., Johnson, W. E., Lark-Horovitz, K., and Siegel, S., 1948, Neutron-bombarded germanium semiconductors. *Phys. Rev.* (2), **74,** 1255, (A) ; see also U.S. Report AECD-2054.

Denney, J. M., 1953, Radiation-damage energy threshold in a face-centred cubic alloy. *Phys. Rev.* (2), **92,** 531, (A) ; 1954 b, Displacement energy of face-centred cubic iron. U.S. Report NAA-SR-271, 26 p ; 1954 b, Experimental evidence for melted regions in metal crystals resulting from particle bombardment. *Phys. Rev.* (2), **94,** 1417, (A).

Dieckamp, H., 1955, Shear modulus recovery of electron irradiated copper. *Phys. Rev.* (2), **98,** 1531, (A).

Dieckamp, H., and Crittenden, E. C., Jr., 1954, Shear modulus of irradiated copper. *Phys. Rev.,* **94,** 1418, (A).

Dienes, G. J., 1952 a, A theoretical estimate of the effect of radiation on elastic constants of simple metals. *Phys. Rev.* (2), **86,** 228 ; 1952 b, Effect of radiation on elastic constants. *Ibid.,* **87,** 666 ; 1953 a, Radiation effects in solids. *Ann. Rev. Nuclear Science,* **2,** 187 ; 1953 b, Effects of nuclear radiations on the mechanical properties of solids. *J. Appl. Phys.,* **24,** 666 ; see also U.S. Report BNL-1340 ; 1953 c, Variable activation energy and the motion of lattice defects. *Phys. Rev.* (2), **91,** 1283.

Dienes, G. J., and Kleinman, D. A., 1953, Nature of radiation damage in diamond. *Phys. Rev.* (2), **91,** 238, (A).

Dixon, C. E., and Bowen, D. B., 1954, Radiation ordering by cyclotron particles. *Phys. Rev.* (2), **94,** 1418, (A).

Dixon, C. E., and Meechan, C. J., 1953, Hardness change in Cu irradiated with 1·25-Mev electrons. *Phys. Rev.* (2), **91,** 237, (A).

Dixon, C. E., Meechan, C. J., and Brinkman, J. A., 1953, Bombardment of ordered Cu$_3$Au by 1 Mev electrons. *Phil. Mag.,* (7) **44,** 449.

Dugdale, R. A., 1952, The extra electrical resistance due to cold work and neutron irradiation of platinum. *Phil. Mag.* (7), **43,** 912 ; 1955, Recent experiments at Harwell on irradiation effects in crystalline solids. *Report of the Conference on Defects in Crystalline Solids,* Bristol 1954 (London : Physical Society), p. 246.

Dugdale, R. A., and Green, A., 1954, Some ordering effects in Cu$_3$Au at about 100°c. *Phil. Mag.* (7), **45,** 163.

Duhamel, F., Freymann, M., and Freymann, R., 1953, Une nouvelle méthode d'étude de certains effets physicochimiques de l'irradiation dans les piles : la mesure de l'absorption hertzienne des solides. *Comptes Rendus Acad. Sci.,* **237,** 1684.

Eggen, D. T., and Laubenstein, M. J., 1953, Displacement energy for radiation damage in copper. *Phys. Rev.* (2), **91,** 238, (A).

EGGLESTON, R. R., 1952, Cold work studies on copper at low temperatures. *J. Appl. Phys.*, **23,** 1400 ; 1953 a, Annealing of radiation damage effects in copper. *Phys. Rev.* (2), **92,** 531, (A) ; 1953 b, The annealing of copper after radiation damage at low temperatures. *Acta Metallurgica*, **1,** 679.

EGGLESTON, R. R., and BOWMAN, F. E., 1953, Radiation damage of beta-brass. *J. Appl. Phys.*, **24,** 229.

ELLIS, W. C., and GREINER, E. S., 1953, Production of acceptor centres in germanium and silicon by plastic deformation. *Phys. Rev.* (2), **92,** 1061.

FAN, H. Y., 1952, Infrared absorption of nucleon-bombarded silicon II. *Phys. Rev.* (2), **85,** 730, (A).

FAN, H. Y., and BECKER, M., 1951, Infrared optical properties of silicon and germanium. *Reading Conference on Semi-conducting Materials* (London ; Butterworth), p. 132.

FAN, H. Y., and LARK-HOROVITZ, K., 1955, Fast particle irradiation of germanium semiconductors. *Report of the Conference on Defects in Crystalline Solids.* Bristol, 1954 (London : Physical Society), p. 232.

FILLNOW, HALTEMAN, E. K., and MECHLIN, G. F., 1953, X-ray and metallurgical studies on neutron irradiated $Cu_3Au$. *Phys. Rev.* (2), **91,** 236, (A).

FLEEMAN, J., 1953, Effect of neutron irradiation on the phase change in tin. *Phys. Rev.* (2), **91,** 237, (A) ; 1954, The $\beta \rightarrow \alpha$ transformation in tin. *Ibid.* (2), **94,** 1422, (A).

FLEEMAN, J., and DIENES, G. J., 1955, Effect of reactor irradiation on the white-to-grey tin transformation. *J. Appl. Phys.*, **26,** 652.

FLETCHER, R. C., and BROWN, W. L., 1953, Annealing of bombardment damage in a diamond type lattice : theoretical. *Phys. Rev.* (2), **92,** 585.

FLETCHER, R. C., BROWN, W. L., and MACHLUP, S., 1953, Annealing of bombardment damage in germanium : theoretical. *Phys. Rev.* (2), **91,** 237, (A).

FLETCHER, R. C., BROWN, W. L., and WRIGHT, K. A., 1954, The absence of bombardment annealing in the electron bombardment of germanium. *Phys. Rev.* (2), **96,** 833, (A).

FLORIDA, C. D., HOLT, F. R., and STEPHEN, J. H., 1954, Irradiation of transistors. *Nature, Lond.*, **173,** 397.

FORSTER, J. H., FAN, H. Y., and LARK-HOROVITZ, K., 1952, Conductivity of deuteron irradiated germanium and silicon. *Phys. Rev.* (2), **86,** 643, (A). 1953, Deuteron irradiation of germanium near liquid nitrogen temperature. *Ibid.* (2), **91,** 229, (A).

FRANKL, D. R., 1953, The internal friction of rock salt single crystals. *Phys. Rev.* (2), **92,** 573.

FRANKL, D. R., and READ, T. A., 1953, Effects of F-centers on the internal friction of rock salt single crystals. *Phys. Rev.* (2), **89,** 663.

FRENKEL, J., and KONTOROVA, T., 1939, *J. Phys. U.S.S.R.*, **1,** 137 ; referred to by Paneth (1950).

FUES, E., and STUMPF, H., 1955, Klassische nichtlineare Gitterstatik gestörter Kristallstrukturen. *Zeit. Naturforsch.*, **10a,** 136.

GEIB, I. G., and GRACE, R. E., 1952 a, Hardness of deuteron irradiated molybdenum. *Phys. Rev.* (2), **86,** 643, (A) ; erratum, *ibid.*, 638 ; 1952 b, Hardness of deuteron irradiated molybdenum. U.S. Report AECU-2225, 14.

GLICK, H. L., BROOKS, F. C., WITZIG, W. F., and JOHNSON, W. E., 1952, The resistivity of $Cu_3Au$ during neutron irradiation. *Phys. Rev.*, **87,** 1074 ; see also U.S. Report WAPD-T7.

GLICK, H. L., and WITZIG, W. F., 1953, Additional data on the resistivity of $Cu_3Au$ during neutron irradiation. *Phys. Rev.* (2), **91,** 236, (A).

Gordon, R. B., and Nowick, A. S., 1955, Elastic modulus of x-irradiated rock salt. *Phys. Rev.* (2), **98,** 1540, (A).

Gossick, B. R., 1952, Measurements of creep, Young's modulus and yield strength. U.S. Report AECU-2225, 34; 1953, Design of extensometer for creep studies. U.S. Report COO-103.

Griffiths, J. H. E., Owen, J., and Ward, I. M., 1954, Paramagnetic resonance in neutron irradiated diamond and smoky quartz. *Nature, Lond.,* **173,** 439; 1955, Magnetic resonance in irradiated diamond and quartz. *Report of the Conference on Defects in Crystalline Solids*, Bristol, 1954 (London: Physical Society), p. 81.

Harmon, T. C., Eidam, R., and Geib, I. G., 1953, Hardness measurements of molybdenum before and after bombardment. U.S. Report COO-102, 1.

Harmon, T. C., Horvath, L., and Geib, I. G., 1953, Hardness of deuteron irradiated molybdenum. U.S. Report COO-104, 17.

Harris, E. G., 1955, Disordering of polyatomic solids by neutrons. *Phys. Rev.* (2), **98,** 1151, (A).

Harrison, W. A., and Seitz, F., 1955, On the theory of radiation damage. *Phys. Rev.* (2), **98,** 1530, (A).

Hayes, S., and Smoluchowski, R., 1953, Small angle x-ray scattering in proton-irradiated diamond. *Phys. Rev.* (2), **91,** 244, (A).

Henderson, J. W., Cooper, H. G., and Marx, J. W., 1952, Analysis of the resistivity changes produced by irradiation of copper, silver and gold. *Phys. Rev.* (2), **86,** 642, (A).

Hoffman, R. W., and Rasor, N. S., 1954, Annealing kinetics of lattice imperfections using evaporated metal films. *Phys. Rev.* (2), **94,** 1406, (A).

Holden, A. N., and Kunz, F. W., 1954, A model for radiation damaged ductile metals. U.S. Report AECD-3616, 24 p.; referred to in *Nuclear Science Abstracts.*

Holland, H. D., and Gottfried, D., 1955, The effect of nuclear radiation on the structure of zircon. *Acta Cryst.,* **8,** 291.

Huffman, J. R., 1954, The materials testing reactor. *Nucleonics,* **12,** 4, 20.

Huntington, H. B., 1942, Self-consistent treatment of the vacancy mechanism for metallic diffusion. *Phys. Rev.* (2), **61,** 325; 1953, Mobility of interstitial atoms in a face-centered metal. *Ibid.* (2), **91,** 1092; 1954, Creation of displacements in radiation damage. *Ibid.* (2), **93,** 1414.

Hurley, P. M., and Fairburn, H. W., 1952, Alpha-radiation damage in zircon. *J. Appl. Phys.,* **23,** 1408; 1953, Radiation damage in zircon: a possible age method. *Bull. Geol. Soc. Amer.,* **64,** 659.

James, H. M., and Lark-Horovitz, K., 1951, Localized electronic states in bombarded semiconductors. *Zeit. phys. Chem.,* **198,** 107; see also U.S. Report TID-5011.

Jamison, R. E., and Blewitt, T. H., 1952, Slip lines in pile irradiated copper single crystals. *Phys. Rev.* (2), **86,** 641, (A); 1953 a, Some deformation characteristics of reactor irradiated copper single crystals at 78°K and 300°K. *Ibid.* (2), **91,** 237, (A); 1953 b, Behaviour of two types of thermocouples under pile irradiation at low temperatures. *Rev. Sci. Instrum.,* **24,** 474.

Jeppson, M. R., Mather, R. L., Andrew, A., and Yockey, H. P., 1955, Creep of aluminum under cyclotron irradiation. *J. Appl. Phys.,* **26,** 365.

Jeppson, M. R., Mather, R. L., and Yockey, H. P., 1954, Effect of cyclotron irradiation on creep of aluminum. U.S. Report AECD-3631, 30p.

Johnson, F. B., and Pease, R. S., 1954, The pile irradiation of quartz crystal oscillators. *Phil. Mag.* (7), **45,** 651.

Johnson, R. D., and Martin, A. B., 1952, The effect of cyclotron bombardment on self-diffusion in silver. *J. Appl. Phys.*, **23,** 1245.

Johnson, W. E., and Lark-Horovitz, K., 1949, Neutron irradiated semiconductors. *Phys. Rev.* (2), **76,** 442.

Johnston, D. F., 1955, A calculation of the density of electron-trapping defects in neutron-irradiated graphite from measurements of the temperature variation of the Hall coefficient. *J. Nuclear Energy*, **1,** 311.

Jones, E. R. W., Munro, W., and Hancock, N. H., 1951, The creep of aluminium in the N.R.X. pile. British Report AERE M/R 795; 1954, The creep of aluminium during neutron irradiation. *J. Nuclear Energy*, **1,** 76.

Jongenburger, P., 1953, The extra-resistivity owing to vacancies in copper. *Phys. Rev.* (2), **90,** 710.

Kauffman, J. W., and Koehler, J. S., 1952, The quenching-in of lattice vacancies in pure gold. *Phys. Rev.* (2), **88,** 149; 1955, Quenching-in of lattice vacancies in pure gold. *Ibid.* (2), **97,** 555.

Keating, D. T., 1954 a, Diffraction studies of possible ordering in α-brass. *Phys. Rev.* (2), **94,** 1429, (A); 1954 b, Diffraction studies of possible ordering in α-brass. *Acta Metallurgica*, **2,** 885; see also U.S. Report BNL-1848, 9p.; 1955 a, x-ray measurements of pile-irradiated LiF. *Phys. Rev.* (2), **97,** 832; 1955 b, x-ray measurements on low-temperature neutron-irradiated graphite. *Ibid.* (2), **98,** 1859.

Keesom, P. H., Lark-Horovitz, K., and Pearlman, N., 1952 a, The influence of neutron bombardment on the low temperature atomic heat of silicon. *Phys. Rev.* (2), **89,** 900, (A); 1952 b, The effect of neutron bombardment on the low temperature atomic heat of silicon. *Science*, **116,** 630; 1953, The influence of neutron bombardment on the low temperature atomic heat of silicon. U.S. Report COO-102, 8.

Kelly, E. M., 1954, Electron microscope study of slip bands in radiation damaged aluminum crystals. U.S. Report NAA-SR-261, 15p.; 1955, Electron microscope study of slip bands in radiation-damaged aluminum crystals. *Acta Metallurgica*, **3,** 101.

Kierstead, H. A., 1955, Expansion of copper bombarded by 19 mev deuterons. *Phys. Rev.* (2), **98,** 245, (A).

Kinchin, G. H., 1954, Changes in the electrical properties of graphite due to neutron irradiation. *J. Nuclear Energy*, **1,** 124.

Kinchin, G. H., and Pease, R. S., 1955 a, The mechanism of the irradiation disordering of alloys. *J. Nuclear Energy*, **1,** 200; 1955 b, The displacement of atoms in solids by radiation. *Rep. Progress Phys.*, **18,** 1.

Klemens, P. G., 1951, The thermal conductivity of dielectric solids at low temperatures. *Proc. Roy. Soc.* A, **208,** 108.

Klontz, E. E., 1952, Production of lattice defects in germanium by electron bombardment. U.S. Report AECU-2267 or AECU-2664; 1953 a, Electron bombardment of germanium. U.S. Report COO-102, 28; 1953 b, Resistance changes in germanium single crystals during electron bombardment. U.S. Report COO-104, 13.

Klontz, E. E., and Lark-Horovitz, K., 1951, Electron bombardment of Ge. *Phys. Rev.*, **82,** 763, (A); 1952 a, Electron bombardment of semiconductors. U.S. Report AECU-2225, 56; 1952 b, Displacements produced by electron bombardment of germanium. *Phys. Rev.* (2), **86,** 643, (A).

Klontz, E. E., Pepper, R. R., and Lark-Horovitz, K., 1955, Electrical properties of electron bombarded Ge. *Phys. Rev.* (2), **98,** 1535, (A).

Koehler, J. S., 1953, Progress report No. 4. U.S. Report COO-197; 1954, Progress report No. 5. U.S. Report COO-199.

Koehler, J. S., and Seitz, F., 1954, Radiation disarrangement of crystals. *Zeit. Physik*, **138,** 238; 1955, Radiation disarrangement of crystals. *Report of the Conference on Defects in Crystalline Solids*, Bristol, 1954 (London: Physical Society), p. 222.

Kohn, W., 1954, Bombardment damage of Ge crystals by fast electrons. *Phys. Rev.* (2), **94,** 1409, (A).

Kunz, F. W., and Holden, A. N., 1954 a, The effect of short time moderate flux neutron irradiation on the mechanical properties of some metals. *Phys. Rev.* (2), **94,** 1417, (A); 1954 b, The effect of short-time moderate flux neutron irradiations on the mechanical properties of some metals. *Acta Metallurgica*, **2,** 816; see also U.S. Report KAPL-1066, 45 p.

Lark-Horovitz, K., 1951, Nucleon bombarded semi-conductors. *Reading Conference on Semi-conducting Materials* (London: Butterworth), p. 47; 1952, Summary [of work done at Purdue University 1951–52]. U.S. Report AECU-2225, 1.

Lark-Horovitz, K., Becker, M., Davis, R. E., and Fan, H. Y., 1950, Nucleon bombarded silicon. *Phys. Rev.* (2), **78,** 334, (A).

Lark-Horovitz, K., Bleuler, E., Davis, R. E., and Tendam, D., 1948, Deuteron bombarded semi-conductors. *Phys. Rev.* (2), **73,** 1256, (A).

Lawrance, R., Gibson, A. F., and Granville, J. W., 1954, On the current gain of germanium filamentary transistors. *Proc. Phys. Soc.* B, **67,** 625.

Leeser, D. O., 1952, How atomic radiation affects engineering materials. *Materials and Methods*, **36,** 1, 75; 1954, How nuclear radiation affects engineering materials. *Ibid.*, **40,** 2, 110.

Leivo, W. J., 1953, Density changes in proton irradiated potassium chloride. *Phys. Rev.* (2), **91,** 245, (A).

Leivo, W. J., and Smoluchowski, R., 1954, x-ray coloring of 400 mev proton irradiated KCl. *Phys. Rev.* (2), **93,** 1415.

Li, C. Y., and Nowick, A. S., 1955, Effect of quenching and neutron irradiation on atomic mobility in a Cu–Al alloy. *Phys. Rev.* (2), **98,** 1531, (A).

Lin, L.-Y., and Russell, B. R., 1955, Change in length of alkali halide crystals caused by x-ray irradiation. *Phys. Rev.* (2), **99,** 657, (A).

Lipson, H. G., Burstein, E., and Smith, P. L., 1955, Optical effects in plastically deformed germanium. *Phys. Rev.* (2), **98,** 1535, (A).

Loferski, J. J., and Rappaport, P., 1955, Electron voltaic study of electron bombardment damage and its thresholds in Ge and Si. *Phys. Rev.* (2), **98,** 1861.

Lomer, W. M., 1954, Diffusion coefficients in copper under fast neutron irradiation. British Report AERE T/R 1540, 10 p.

Lomer, W. M., and Cottrell, A. H., 1955, Annealing of point defects in metals and alloys. *Phil. Mag.* (7), **46,** 711.

McClelland, J. D., 1953, Effect of neutron bombardment upon the magnetic susceptibility of various oxides. U.S. Report NAA-SR-263, 14 p.

McClelland, J. D., and Donoghue, J. J., 1953, The effect of neutron bombardment upon the magnetic susceptibility of several pure oxides. *J. Appl. Phys.*, **24,** 963.

McDonnell, W. R., and Kierstead, H. A., 1954, Expansion of copper bombarded by 21-mev deuterons. *Phys. Rev.* (2), **93,** 247; erratum, *ibid.*, **98,** 1870.

McReynolds, A. W., Augustyniak, W., McKeown, M., and Rosenblatt, D. B., 1954, Neutron irradiation effects at low temperature—Cu and Al. *Phys. Rev.* (2), **94,** 1417, (A); 1955, Neutron irradiation effects in Cu and Al at 80°K. *Ibid.* (2), **98,** 418.

Maddin, R., and Cottrell, A. H., 1955, Quench hardening of aluminium single crystals. *Phil. Mag.* (7), **46,** 735.

MAIER, M. S., and NELSON, H. R., 1942, Self-diffusion in copper. *Trans. A.I.M.E.*, **147,** 39.

MAKIN, M. J., 1954, Effect of alpha-particle bombardment on creep in cadmium single crystals. *Nature, Lond.*, **174,** 752 ; 1955, The effect of alpha-particle bombardment on the creep of cadmium single crystals. *J. Nuclear Energy*, **1,** 181.

MANINTVELD, J. A., 1952, Recovery of the resistivity of metals after cold-working. *Nature, Lond.*, **169,** 623.

MAPOTHER, D., 1953, Effect of x-irradiation on the self-diffusion coefficient of sodium in sodium chloride. *Phys. Rev.* (2). **89,** 1231.

MARKHAM, J. J., 1952, Speculation on the formation of F-centers during irradiation. *Phys. Rev.* (2), **88,** 500.

MARTIN, A. B., AUSTERMAN, S. B., EGGLESTON, R. R., MCGEE, J. F., and TARPINIAN, M., 1951, The effect of cyclotron bombardment of the physical properties of metals. *Phys. Rev.* (2), **81,** 664, (A).

MARX, J. W., 1953, Radiation damage and rate processes. *Phys. Rev.* (2), **91,** 1564.

MARX, J. W., COOPER, H. G., and HENDERSON, J. W., 1952, Radiation damage and recovery in Cu, Ag, Au, Ni and Ta. *Phys. Rev.* (2), **88,** 106 ; see also U.S. Report AECU-2118, 19 p.

MARX, J. W., KOEHLER, J. S., and WERT, C., 1952, Effect of deuteron bombardment on the electrical resistivity of copper, silver, and gold. *Phys. Rev.* (2), **86,** 643, (A).

MAYBURG, S., 1954, Vacancies and interstitials in heat treated germanium. *Phys. Rev.* (2), **95,** 38.

MEECHAN, C. J., and DIECKAMP, G. M., 1955, On the recovery of electrical resistance of cold-worked gold. U.S. Report NAA-SR-1159.

MEECHAN, C. J., and EGGLESTON, R. R., 1954, Formation energies of vacancies in copper and gold. *Acta Metallurgica,* **2,** 680.

MEYER, R. A., 1954, Influence of deuteron bombardment and strain hardening on notch sensitivity of mild steel. *J. Appl. Phys,*, **25,** 1369 ; see also U.S. Report USNRDL-431, 56 p.

MONGINI, L., 1953, Effeti delle radiazioni nucleari sulla resistività elettrica e durezza dei metalli. *Energia Nucleare*, No. 8, 209.

MURRAY, G. T., and TAYLOR, W. E., 1952, Neutron bombardment of a copper–beryllium alloy. *Phys. Rev.* (2), **86,** 642, (A) ; 1953, Effect of neutron irradiation on supersaturated solid solutions of beryllium in copper. U.S. Report ORNL-1323 ; 1954, Effect of neutron irradiation on supersaturated solid solutions of beryllium in copper. *Acta Metallurgica,* **2,** 52.

NABARRO, F. R. N., 1948, Deformation of crystals by the motion of single ions. *Report of the Conference on the Strength of Solids*, Bristol, 1947 (London : Physical Society), p. 75 ; 1952, Effect of radiation on elastic constants. *Phys. Rev.* (2), **87,** 665.

NELSON, C. M., SPROULL, R. L., and CASWELL, R. S., 1953, Conductivity changes in KCl produced by $\gamma$ and n irradiation. *Phys. Rev.* (2), **90,** 364, (A).

O'BRIEN, M. C. M., and PRYCE, M. H. L., 1955, Paramagnetic resonance in irradiated diamond and quartz : interpretation. *Report of the Conference on Defects in Crystalline Solids*, Bristol, 1954 (London : Physical Society), p. 88.

O'CONNOR, J. J., and FOSTER, L. S., 1954, A nuclear reactor for metallurgical research. *Nuclear Engineering*, Part II, Chem. Eng. Progr. Symposium Ser., **50,** 12, 59.

ODENCRANTZ, F. K., 1952, Alpha-particle bombardment of PbS semiconductors. *Phys. Rev.* (2), **88,** 166, (A).

Otley, K. O., 1952, Effects of high-energy radiation upon glasses. *Glass Ind.*, **33**, 24.

Overhauser, A. W., 1953 a, Annealing effects in irradiated copper. *Phys. Rev.* (2), **92**, 530, (A) ; 1953 b, Isothermal annealing effects in irradiated copper. *Ibid.* (2), **90**, 393 ; see also U.S. Report AECU-2358 ; 1954, Stored energy measurements in irradiated copper. *Ibid.* (2), **94**, 1551.

Ozeroff, J., 1949, Atomic displacements produced by fission fragments and fission neutrons in matter. U.S. Report AECD-2973 (KAPL-205), 42 p.

Palladino, N. J., 1954, Information pertaining to the use of thermocouples in high neutron flux. U.S. Report WAPD-ReS-13, 2 p., referred to in *Nuclear Science Abstracts*.

Paneth, H. R., 1950, The mechanism of self-diffusion in alkali metals. *Phys. Rev.* (2), **80**, 708.

Pearlstein, E. A., 1953 a, Changes in conductivity of NaCl produced by bombardment with 360 mev protons. *Phys. Rev.* (2), **91**, 244, (A) ; 1953 b, Change of electrical conductivity of sodium chloride upon bombardment with high energy protons. *Phys. Rev.* (2), **92**, 881 ; see also U.S. Report NYO-3127 ; 1954, Change of electrical conductivity of alkali halides upon irradiation with 350 mev protons. *Phys. Rev.* (2), **94**, 1402, (A).

Pearlstein, E. A., Ingham, H., and Smoluchowski, R., 1955, Energy dependence of radiation effects in solids. *Phys. Rev.* (2), **98**, 1530, (A).

Pease, R. S., 1954, x-ray examination of irradiation effects in boron compounds. *Acta Cryst.*, **7**, 663, (A).

Pepper, R., Klontz, E. E., Lark-Horovitz, K., and MacKay, J., 1954, Hall and resistivity measurements during electron bombardment of germanium and indium–antimony. *Phys. Rev.* (2), **94**, 1410, (A).

Pigg, J. C., Cleland, J. W., Crawford, J. H. Jr., and Lark-Horovitz, K., 1951, Pile irradiation of semiconducting $Cu_2O$. *Phys. Rev.* (2), **82**, 763, (A).

Pizarro, R. A., 1952, Preliminary outline of creep testing machine design project. U.S. Report AECU-2225, 37.

Pratt, P. L., 1955, The interaction of colour-centres and vacancies with dislocations in alkali halide crystals. *Report of the Conference on Defects in Crystalline Solids*, Bristol, 1954 (London : Physical Society), p. 402.

Primak, W., 1954, The metamict state. *Phys. Rev.* (2), **95**, 837 ; 1955, Experimental evidence for thermal spikes in radiation damage. *Ibid.* (2), **98**, 1854.

Primak, W., Delbecq, C. J., and Yuster, P. H., 1955, Photoelastic observations of the expansion of alkali halides on irradiation. *Phys. Rev.* (2), **98**, 1708.

Primak, W., Fuchs, L. H., and Day, P., 1953, Radiation damage in insulators. *Phys. Rev.* (2), **92**, 1064.

Primak, W., Yuster, P. H., and Delbecq, C. J., 1955, Photoelastic observation of the expansion of alkali halides on irradiation. *Phys. Rev.* (2), **98**, 237, (A).

Przibram, K., 1953, *Verfärbung und Lumineszenz.* (Wien : Springer), 275 p.

Randolph, B. W., 1952, Temperature dependence of the resistivity of deuteron irradiated and annealed molybdenum. *Phys. Rev.* (2), **85**, 710, (A) ; 1953, Electrical measurements on molybdenum. U.S. Report COO-102, 24.

Rappaport, P., 1954 a, The electron–voltaic effect in *p-n* junctions induced by beta-particle bombardment. *Phys. Rev.* (2), **93**, 246 ; 1954 b, Minority carrier lifetime in semiconductors as a sensitive indicator of radiation damage. *Ibid.* (2), **94**, 1409, (A).

RASOR, N. S., 1955, Annealing kinetics of lattice defects in evaporated copper films. *Phys. Rev.* (2), **98,** 1555, (A).

REDMAN, J. K., COLTMAN, R. R., and BLEWITT, T. H., 1953, The activation energy for the recovery of reactor irradiated copper crystals. *Phys. Rev.* (2), **91,** 448, (A).

RICHARDS, J. T., 1955, Effect of irradiation upon beryllium copper. *Acta Metallurgica,* **3,** 211.

ROBINSON, W. H., LI, Y.-Y., and SMOLUCHOWSKI, R., 1954, Small-angle scattering of x-rays by irradiated diamond. *Phys. Rev.* (2), **94,** 1435, (A).

RODEBACK, G. W., 1954, Imperfections in copper in terms of electrical resistivity and thermoelectric power. *Phys. Rev.* (2), **94,** 1406, (A).

ROSENBLATT, D. B., SMOLUCHOWSKI, R., and DIENES, G. J., 1954, Radiation induced changes in the electrical resistance of $\alpha$-brass. *Phys. Rev.* (2), **94,** 1417, (A).

ROSWELL, A. E., and NOWICK, A. S., 1953, Decay of lattice defects frozen into an alloy by quenching. *J. Metals,* **5** (*Trans. A.I.M.E.,* **197**), 1259.

ROTHSTEIN, J., 1953 a, Solids subjected to a constant rate of generation of lattice defects. *Phys. Rev.* (2), **89,** 901, (A) ; 1953 b, Solids subjected to a constant rate of generation of lattice defects. U.S. Report SCEL-E-1127, AD-25284, 76 p.

SAMPSON, J. B., HURWITZ, H., Jr., and CLANCY, E. F., 1955, Sensitivity of radiation damage to the displacement probability. *Phys. Rev.* (2), **99,** in the press, (A).

SCHMID, E., and LINTER, K., 1954 a, Über die Bedeutung eines Bombardments von Korpuskularstrahlen für die Plastizität von Metallkristallen. *Anzeiger Österr. Akad. Wiss., Math.-Naturwiss. Klasse,* **91,** 25 ; 1954 b, Über die Bedeutung eines Bombardments mit Korpuskularstrahlen für die Plastizität von Metallkristallen. *Sitz.-Ber. Österr. Akad. Wiss.* (II), **163,** 109.

SCHULZ-DUBOIS, E., NISENOFF, M., FAN, H. Y., and LARK-HOROVITZ, K., 1955, Spin resonance in neutron irradiated silicon. *Phys. Rev.* (2), **98,** 1561, (A).

SCHWED, P., and GROETZINGER, G., 1952, Considerations regarding the distribution of radiation damage in matter bombarded by light ions and a method of making it uniform. *J. Appl. Phys.,* **23,** 234.

SEEGER, A., 1955, Bestrahlungsfehlordnung und Diffusionsvorgänge in Edelmetallen. *Zeit. Naturforsch.,* **10a,** 251.

SEITZ, F., 1949, On the disordering of solids by action of fact massive particles. *Disc. Faraday Soc.,* No. 5, 271 ; 1952, Radiation effects in solids. *Physics Today,* **5,** 6, 6 ; 1955, Source of disordering of alloys under irradiation. *Phys. Rev.* (2), **98,** 1530, (A).

SHULMAN, R. G., BROWN, W. L., and FLETCHER, R. C., 1954, Hole trapping due to lattice defects in germanium. *Phys. Rev.* (2), **96,** 833, (A).

SIDHU, S. S., and HENRY, C. O., 1950, Effect of high energy neutron bombardment on crystal lattice of beryllium, graphite, diamond, and aluminum. *Phys. Rev.* (2), **80,** 123, (A).

SIEGEL, S., 1949, Effect of neutron bombardment on order in the alloy $Cu_3Au$. *Phys. Rev.* (2), **75,** 1823.

SLATER, J. C., 1951, Effects of radiation on materials. *J. Appl. Phys.,* **22,** 237.

SMART, J. S., Jr., SMITH, A. A., Jr., and PHILLIPS, A. J., 1941, Preparation and some properties of high purity copper. *Trans. A.I.M.E.,* **143,** 272.

SMITH, W. J., LEIVO, W. J., and SMOLUCHOWSKI, R., 1954, Interferometric study of the surface of x-ray and proton irradiated KCl crystals. *Phys. Rev.* (2), **94,** 1435, (A).

Smoluchowski, R., 1954, On the influence of nuclear radiation on electrical conductivity of alkali halides. *Phys. Rev.* (2), **94**, 1409, (A) ; 1955, Behaviour of defects in alkali halides produced by high energy protons and gamma rays. *Report of the Conference on Defects in Crystalline Solids*, Bristol, 1954 (London : Physical Society), p. 252.

Smoluchowski, R., Pearlstein, E., and Ingham, H., 1955, Radiation effects in solids produced by nuclear disintegrations. *Phys. Rev.* (2), **98**, 1530, (A).

Smoluchowski, R., Leivo, W. J., Pearlstein, E. A., Smith, W. J., and Vaughan, W., 1953, Progress report for May 1, 1952–May 1, 1953. U.S. Report NYO-3126.

Snyder, W. S., and Neufeld, J., 1954, On the disordering of solids by heavy corpuscular radiation. *Phys. Rev.* (2), **94**, 760, (A) ; 1955, Disordering of solids by neutron radiation. *Phys. Rev.* (2), **97**, 1636.

Steele, R. V., and Wallace, W. P., 1954, The effect of neutron flux on the mechanical properties of aluminum alloys. U.S. Report LRL-145, 21 p.

Stello, P. G., 1952, Relative ordering rates in the superlattice alloy AuCu. U.S. Report NAA-SR-171.

Stevens, D. K., 1954, Magnetic susceptibility of annealed and fast neutron bombarded germanium. U.S. Report ORNL-1599, 37 p. ; 1955, Magnetic susceptibility of fast neutron bombarded crystalline quartz. *Phys. Rev.* (2), **98**, 1541, (A).

Stevens, D. K., Cleland, J. W., and Crawford, J. H., Jr., 1954, Magnetic susceptibility of fast neutron bombarded Ge. *Phys, Rev.* (2), **94**, 1409, (A).

Stoeckman, F., Klontz, E. E., Fan, H. Y., and Lark-Horovitz, K., 1955, Photoconductivity of electron-bombarded Ge. *Phys. Rev.* (2), **98**, 1535, (A).

Sutton, C. R., and Leeser, D. O., 1954 a, Radiation effects on structural materials. *Nuclear Engineering*, Part II, Chem. Eng. Progr. Symposium Ser., 50, 12, 208 ; 1954 b, Radiation effects on reactor materials : metals. *Nucleonics*, **12**, 9, 8.

Taylor, W. E., 1952, Comparison of thermally induced lattice defects in germanium and silicon with defects produced by nucleon bombardment. *Phys. Rev.* (2), **86**, 642, (A).

Taylor, W. E., Odell, N. H., and Fan, H. Y., 1952, Grain-boundary barriers in germanium. *Phys. Rev.* (2), **88**, 867.

Tucker, C. W., Jr., and Sampson, J. B., 1954, Interstitial content of radiation damaged metals from precision x-ray lattice parameter measurements. *Phys. Rev.* (2), **94**, 1418, (A) ; 1955, Interstitial content of radiation-damaged metals I. Principles of the measurements. *Acta Metallurgica*, **2**, 433 ; see also U.S. Report KAPL-1037.

Tucker, C. W., Jr., and Senio, P., 1954 a, x-ray scattering by lattice defects in neutron-irradiated single crystals of boron carbide. *Acta Cryst.*, **7**, 456 ; see also U.S. Report AECD-3613, 7 p. ; 1954 b, x-ray scattering by neutron irradiated single crystals of boron carbide. Part I. U.S. Report KAPL-1180, 37 p. ; 1955 a, x-ray scattering effects in irradiated boron carbide. *Phys. Rev.* (2), **98**, 1541, (A) ; 1955 b, x-ray scattering by neutron irradiated single crystals of boron carbide. *Acta Cryst.*, **8**, 371.

Varley, J. H. O., 1954 a, A mechanism for the displacement of ions in an ionic lattice. *Nature, Lond.*, **174**, 886 ; 1954 b, A new interpretation of irradiation-induced phenomena in alkali halides. *J. Nuclear Energy*, **1**, 130 ; see also AERE M/R 1508, 12 p.

VAUGHAN, W. H., LEIVO, W. J., and SMOLUCHOWSKI, R., 1953, Mechanical. properties of proton irradiated alkali halides. *Phys. Rev.* (2), **91,** 245, (A).

WARREN, B. E., 1951, x-ray study of radiation damage. U.S. Report NYO-767, 4 p. ; 1952, x-ray study of radiation damage. U.S. Reports NYO-3731 and NYO-3732 ; 1953, x-ray study of radiation damage. U.S. Report NYO-3734 ; 1954, x-ray study of irradiation damage. U.S. Reports NYO-6508, 6 p., and NYO-6511, 5 p.

WEISSMANN, S., and CHANG, R., 1955, x-ray diffraction studies of radiation damage of germanium single crystals. *Phys. Rev.* (2), **99,** 657, (A).

WESTERVELT, D. R., 1953, Thermal annealing of radiation-induced hardness changes in alkali halides. *Acta Metallurgica,* **1,** 755 ; 1954, Mechancial effects of ionizing radiation in the alkali halides. U.S. Report NAA-SR-888, 26 p.

WITZIG, W. F., 1951, Creep of copper under deuteron bombardment. U.S. Report AECD-3290, WAPD-43 ; 1952 a, Creep of copper under deuteron bombardment. *Phys. Rev.* (2), **87,** 211, (A) ; 1952 b, Creep of copper under deuteron bombardment. *J. Appl. Phys.*, **23,** 1263.

WITTELS, M., 1953, The lattice expansion of quartz due to fast neutron bombardment. *Phys. Rev.* (2), **89,** 656.

WITTLES, M., and SHERRILL, F. A., 1954, Radiation damage in $SiO_2$ structures. *Phys. Rev.* (2), **93,** 1117.

WRUCK, D. A., 1954, Crystal structure as a factor in irradiation damage. U.S. Report AD-25100 ; referred to in *Nuclear Science Abstracts.*

WRUCK, D., and WERT, C., 1954 a, Crystal structure as a factor in radiation damage. *Phys. Rev.* (2), **94,** 1417, (A) ; 1954 b, The role of crystal structure on irradiation effects on metals. U.S. Report AECU-2906, 26 p. ; 1955, The role of crystal structure on irradiation effects in metals. *Acta Metallurgica,* **3,** 115.

YOCKEY, H. P., ANDREW, A., FILLMORE, F. L., GLASGOW, L. E., HUNT, C. d'A., and PEPPER, J. H., 1954, Cyclotron techniques for radiation damage studies. *Rev. Sci. Instrum.*, **25,** 1011.

YOCKEY, H. P., FILLMORE, F. L., HUNT, C. d'A., ANDREW, A., GLASGOW, L. WEBER, F. R., Jr., JEPPSON, M. R., PEPPER, J. H., and CARTER, R. E., 1952, The use of cyclotron irradiation in the study of radiation effects on materials. U.S. Report NAA-SR-186.

*Note added in proof.*—Professor Schmid has brought to my notice two further papers on the effects of radiation on the properties of metals. In the first (Schmid, E., and Lintner, K., 1955, " Über die Bedeutung eines Elektronenbombardments für die Plastizität von Metallkristallen ", *Zeit. Metallk.*, **46,** 71) the effects of electron bombardment on the creep of zinc crystals are reported ; usually a hardening was found. In the second (Neumann, B., and Schmid, E., 1955, " Effekte von Korpuskularbestrahlung an aushärtbaren Legierungen ", *Metall,* **9,** 349) it is reported that resistivity changes are observed in Cu–Be alloys after small $\alpha$ and $\beta$ particle bombardments, although no change of microhardness was found. A review article of radiation damage in German by K. Lintner and E. Schmid will appear in vol. 28 of *Ergebnisse der Exakten Naturwissenschaften.*

We beg to acknowledge the source of the following text-figures :—

Figures 1 and 4 from Cooper, H. G., Koehler, J. S., and Marx, J. W., 1955, *Phys. Rev.*, **97,** 599 (figs. 5 and 8).

Figure 2 from Glick, H. L., Brooks, F. C., Witzig, W. F., and Johnson, W. E., 1952, *Phys. Rev.*, **87,** 1074 (fig. 1).

Figure 3 from Overhauser, A. W., 1954, *Phys. Rev.*, **94,** 1551 (fig. 3).

Figures 5 and 6 from Schmid, E., and Lintner, K., 1954, *Sitz. Österr. Akad. Wiss.*, **163,** 109 (figs. 2 and 5).

Figures 7 and 8 from Bruch, C. A., McHugh, W. E., and Hockenbury, R. W., 1955, *American Institute of Mining and Metallurgical Engineers, J. Metals,* **7,** 281 (figs. 3 and 7).

Figure 9 from Fan, H. Y., and Lark-Horovitz, K., 1955, *Report on the Conference on Defects in Crystalline Solids,* Bristol, 1954 (London : Physical Society), p. 232 (fig. 2).

Figure 10 from James, H. M., and Lark-Horovitz, K., 1951, Akademische Verlagsgesellschaft, Geest & Portig K.-G.

Figure 11 from Klontz, E. E.

Figure 12 from Loferski, J. J., and Rappaport, P., 1955, *Phys. Rev.*, **98,** 1861 (fig. 2).

**Annals of Science**

A QUARTERLY REVIEW OF
THE HISTORY OF SCIENCE
SINCE THE RENAISSANCE

EDITORS

D. McKIE, D.Sc., Ph.D.,
University College, London.

HARCOURT BROWN,
M.A., Ph.D.,
Brown University, Providence, R.I.,
U.S.A.

H. W. ROBINSON,
Former Librarian,
Royal Society of London.

N. H. de V. HEATHCOTE,
B.Sc., Ph.D.,
University College, London.

ANNUAL SUBSCRIPTION
**£3 3s. 0d.**
OR
18s. 0d.
PER PART
POST FREE

ALERE FLAMMAM

ALERE FLAMMAM

**THE MATHEMATICAL WORKS OF JOHN WALLIS, D.D., F.R.S.**

*by*

**J. F. SCOTT, Ph.D., B.A.**

"His work will be indispensable to those interested in the early history of The Royal Society. I commend to all students of the Seventeenth Century, whether scientific or humane, this learned and lucid book."—Extract from foreword by Prof. E. N. da C. Andrade, D.Sc., Ph.D., F.R.S.

**Recommended for publication by University of London**

**12/6** net

*Printed and Published by*
**TAYLOR & FRANCIS, LTD.**
RED LION COURT, FLEET STREET, LONDON, E.C.4.

Jan 6 56

FILED IN STACKS

# *Early Scientific Publications*

ALERE FLAMMAM

**DIARY OF ROBERT HOOKE,** M.A., M.D., F.R.S.
**1672-1680**

Edited by **H. W. ROBINSON** and **W. ADAMS**
**Recommended for publication by the Royal Society, London**

**25/-**
net

"This vivid record of the scientific, artistic and social activities of a remarkable man during remarkable years has too long remained in obscurity."—Extract from foreword by Sir Frederick Gowland Hopkins, O.M., President of the Royal Society.

**MATHEMATICAL WORK OF JOHN WALLIS,** D.D., F.R.S.

By **J. F. SCOTT, Ph.D., B.A.**

**12/6**
net

"His work will be indispensable to those interested in the early history of The Royal Society. I commend to all students of the Seventeenth Century, whether scientific or humane, this learned and lucid book."—Extract from foreword by Prof. E. N. da C. Andrade, D.Sc., Ph.D., F.R.S.
**Recommended for publication by University of London**

**CORRESPONDENCE AND PAPERS OF EDMOND HALLEY**

**21/-**
net

Arranged and Edited by **EUGENE FAIRFIELD MACPIKE**
First published on behalf of The History of Science Society by Oxford University Press. Now re-issued by Taylor & Francis, Ltd.

**MEMOIRS OF SIR ISAAC NEWTON'S LIFE**

**5/-**
net

By **WILLIAM STUKELEY, M.D., F.R.S., 1752**
From an Original Manuscript
Now in the possession of the Royal Society, London

**HEVELIUS, FLAMSTEED AND HALLEY**

**12/6**
net

Three Contemporary Astronomers and their Mutual Relations
By **EUGENE FAIRFIELD MACPIKE**
**Published by arrangement with The History of Science Society**

Established
over 150 years

**TAYLOR & FRANCIS, LTD.**
**RED LION COURT, FLEET ST., LONDON E.C.**
**PRINTERS & PUBLISHERS OF SCIENTIFIC BOOKS**